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DEMETALLIZATION OF HEAVY RESIDUAL OILS

William C. Rovesti, et al

Hydrocarbon Research, Incorporated
Trenton, New Jersey

December 1973

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The report gives results of a program to develop an improved demetallization catalyst so that residuum with high-sulfur and high-metals content could be desulfurized economically. Twenty-eight catalysts were prepared, representing a number of combinations of supports and promoters. Impregnating 20 x 50 mesh granulated activated bauxite with promoters provided the necessary catalytic activity and resistance to poisoning. The residua that were demetallized were Tia Juana, Bachaquero, and Gach Saran vacuum residua. Indications are that these residua can be economically desulfurized to 0.5 weight percent sulfur fuel oil.

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Nickel	
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ABSTRACT

The current energy shortage in the United States, combined with the present and anticipated sulfur dioxide and other pollutant emission standards, have increased the need for and the value of clean, low sulfur fuel oil. Many large crude oil reserves exist in the world which have high sulfur contents and contain nickel and vanadium contaminants in high enough concentrations to rapidly poison hydrodesulfurization catalysts. This combination makes it economically unattractive to desulfurize the residual fraction of these crudes.

The purpose of this program, carried out at the Trenton, New Jersey laboratories of Hydrocarbon Research, Inc., a subsidiary of Dynalectron Corporation, was to develop an improved demetallization catalyst so that desulfurization of the residuum could be carried out economically. A total of twenty-seven catalysts were prepared representing a number of combinations of supports and promoters.

It was found that 20 x 50 mesh granulated activated bauxite when impregnated with a molybdenum promoter provided the necessary catalytic activity and resistance to poisoning.

Demetallization of Tia Juana, Bachaquero, and Gach Saran vacuum residua was carried out and the products of this operation were subsequently desulfurized to produce 0.5 weight percent sulfur fuel oil. Economic analysis of the data indicated that the fuel oil could be produced for \$1.19, \$1.46, and \$1.64 per barrel for the Gach Saran, Tia Juana, and Bachaquero vacuum residua, respectively, in a United States Gulf Coast facility with a capacity of 20,000 barrels per day. These costs include hydrogen, catalyst, all other operating expenses, and capital charges of 25 percent of investment.

CONTENTS

	Page No.
Abstract	iii
List of Figures	vii
List of Tables	xi

SECTIONS

I.	CONCLUSIONS	1
II.	RECOMMENDATIONS	3
III.	INTRODUCTION	5
IV.	EXPERIMENTAL PROGRAM	9
V.	PROCESS ECONOMICS	73
VI.	APPENDICES	83

Preceding page blank

LIST OF FIGURES

Figure No.	Title	Page No.
1	Pore Volume Distribution of Demetallization Catalyst Supports	14
2	Fixed Bed Demetallization Unit	18
3	Fixed Bed Demetallization Reactor	19
4	Alteration of the Pore Volume Distribution of Activated Bauxite During Impregnation with Molybdenum	32
5	Cumulative Pore Size Distribution of Various LX-22 Preparations	33
6	Electron Probe and X-Ray Studies of LX-22-1 at 100X	34
7	Electron Probe and X-Ray Studies of LX-22-5 at 200X	36
8	Demetallization of Tia Juana Vacuum Residuum over 2% Molybdenum/20 x 50 Mesh Bauxite	40
9	Demetallization of Tia Juana Vacuum Residuum over 2% Molybdenum/20 x 50 Mesh Activated Bauxite (HRI 2765)	43
10	Change in Activated Bauxite Pore Size Distribution When Demetallizing Tia Juana Vacuum Residuum	44
11	Change in Pore Size Distribution of LX-22-1 When Demetallizing Tia Juana Vacuum Residuum	46

Preceding page blank

LIST OF FIGURES

Figure No.	Title	Page No.
12	Change in Pore Size Distribution of LX-22-5 When Demetallizing Tia Juana Vacuum Residuum	47
13	Demetallization of Bachaquero Vacuum Residuum over 2% Molybdenum/20 x 50 Mesh Bauxite	48
14	Demetallization of Bachaquero Vacuum Residuum over 2% Molybdenum/20 x 50 Mesh Bauxite	50
15	Change in Pore Size Distribution of LX-22-4 When Demetallizing Bachaquero Vacuum Residuum	51
16	Change in Pore Size Distribution of LX-22-3 When Demetallizing Bachaquero Vacuum Residuum	52
17	Demetallization of Gach Saran Vacuum Residuum over 2% Mo/20 x 50 Mesh Bauxite	53
18	Change in Pore Size Distribution of LX-22-2 When Demetallizing Gach Saran Vacuum Residuum	54
19	Desulfurization of Demetallized Gach Saran Vacuum Residuum	60
20	Desulfurization of Demetallized Bachaquero Vacuum Residuum	61
21	Desulfurization of Demetallized Tia Juana Vacuum Residuum	62

LIST OF FIGURES

Figure No.	Title	Page No.
22	Total Operating Cost: Two-Stage Demetallization-Desulfurization of Gach Saran Vacuum Residuum	74
23	Total Operating Cost: Two-Stage Demetallization-Desulfurization of Tia Juana Vacuum Residuum	76
24	Total Operating Cost: Two-Stage Demetallization-Desulfurization of Bachaquero Vacuum Residuum	77
25	Overall Costs for Producing Low Sulfur Fuel Oil from Bachaquero Vacuum Residuum	78

LIST OF TABLES

Table No.	Title	Page No.
1	Residual Fuel Oil Prices	6
2	Petroleum Demetallization Catalyst Bibliography of U.S. Patents 1954-1973	10
3	Catalyst Supports	13
4	Demetallization Catalysts	16
5	Summary of Demetallization Catalyst Screening Operations Using Tia Juana Vacuum Residuum	22
6	Summary of Demetallization Catalyst Screening Data	28
7	Description and Analyses of the Activated Bauxite Support Used in the Preparation of LX-22 Catalysts	30
8	Molybdenum Content and Compacted Bulk Density of Various LX-22 Preparations	31
9	1971 Vacuum Bottoms Production Rates for Feeds Studied in Program	37
10	Vacuum Residuum Feed Inspections	39
11	Analyses of Spent Demetallization Catalyst	42
12	Composition of Demetallized Residua Fed to the Desulfurization Reactor	56
13	Demetallized Feed Inspections	57

Preceding page blank

LIST OF TABLES

Table No.	Title	Page No.
14	Summary of Inspections on American Cyanamid 0.02" High Activity Beaded Catalyst	58
15	Analyses of Spent Desulfurization Catalyst	63
16	Vanadium and Nickel Balances from Desulfurization Runs	64
17	Effect of Metals Removal from High Metals Feed on Metals Laydown on Catalyst	66
18	Summary of Results on the Demetallization and Desulfurization of Vacuum Residua	67
19	Quantitative N.A.A. Analyses of Vacuum Residua	69
20	Trace Element Analyses	70
21	Trace Metal Analyses on Tia Juana Vacuum Residuum Feed and Selected Demetallized Products Using Neutron Activation and Atomic Absorption Analyses	71
22	Estimated Overall Yields and Product Properties: Consecutive Demetallization and Desulfurization of Gach Saran Vacuum Residuum	80
23	Estimated Overall Yields and Product Properties: Consecutive Demetallization and Desulfurization of Tia Juana Vacuum Residuum	81

LIST OF TABLES

Table No.	Title	Page No.
24	Estimated Overall Yields and Product Properties: Consecutive Demetallization and Desulfurization of Bachaquero Vacuum Residuum	82
C-1	Summary of Catalyst Screening Runs	109
D-1	Summary of Demetallization Runs	117
E-1	Summary of Desulfurization Runs	123
F-1 to F-12	Operating Conditions, Yields, and Product Inspections	129

SECTION I

CONCLUSIONS

In this program, a number of catalyst promoters, mainly from Group VIII of the Periodic Table, were deposited on low cost catalyst supports. Twenty-seven combinations in all were prepared. Evaluation of these catalysts was carried out in a downflow, fixed bed, continuous reactor by measuring the amount of demetallization obtained on Tia Juana vacuum residuum. This residuum was selected for use in the screening procedure because it is a material produced in large volume in Venezuela, has been historically imported to the East Coast of the United States, and has high metals and sulfur concentrations.

Results of the screening tests indicated that 20 x 50 mesh activated bauxite, impregnated with two weight percent molybdenum, provided a catalyst with greatly improved demetallization activity, reasonable stability to poisoning, and relatively low cost. Present day commercial hydrodesulfurization catalysts cost between $0.85 and $1.50 per pound. It appears that this new catalyst can be sold for about $0.20 per pound.

In order to test the overall combination of demetallization followed by desulfurization, quantities of demetallized product were gathered by demetallizing Tia Juana, Bachaquero, and Gach Saran vacuum residua. The first two are major Venezuelan export crudes and the latter is a major Iranian export crude. In 1972, the combined production of these crudes was about 2,000,000 barrels per day. Normally, the residua from these Venezuelan crudes are blended with refined distillates to meet product specifications or are used as ship bunkers. The Iranian crude, however, is exported as whole crude.

The demetallized residua were then desulfurized by a high activity desulfurization catalyst to produce about 96 volume percent yield of 0.5 weight percent sulfur fuel oil (350°F+). Naphtha was the other major product and amounted to about eight percent, which gave an overall liquid yield of about 104 volume percent.

Process economic studies were made and the overall costs for producing 0.5 weight percent sulfur fuel oil, including capital charges of 25 percent, in a United States Gulf Coast unit with a 20,000 barrel per day capacity would be:

Tia Juana	$1.46 per barrel
Bachaquero	$1.64 per barrel
Gach Saran	$1.19 per barrel

These costs are far less than the current differential between 0.5 percent sulfur fuel oil and high sulfur residual oil.

SECTION II

RECOMMENDATIONS

It is recommended that this work be continued by carrying out the work listed below.

1. Long term aging test on catalyst sample promoted with 0.5 weight percent molybdenum to obtain data to provide a comparison with catalyst promoted with 2.0 weight percent molybdenum.

2. Preparation in laboratory equipment of small batches of catalyst by catalyst manufacturers.

3. Screening tests to (a) establish initial activity of catalyst samples, (b) obtain estimates of cost-activity relationships, (c) obtain some short term aging data.

4. Long term aging test on the best laboratory samples evaluated in (3).

5. Production of 5,000-10,000 pounds of catalyst by catalyst manufacturer.

6. Initial screening test on catalyst produced in (5).

7. Long term deactivation studies over commercially produced catalyst using one feed from the original program.

8. Additional two-stage demetallization and desulfurization studies on other feeds with optimization of level of demetallization to be selected from high metals Venezuelan, Canadian, Middle East, or domestic crudes.

If the effort contemplated in the tasks above proves to be successful, it should be followed by a large scale pilot plant demonstration of the demetallization operation. Desulfurization studies of the demetallized product from the pilot operation would then be in order. A detailed commercial plant design based on these results should then be prepared.

SECTION III

INTRODUCTION

The United States has developed a position which is unique in its history in that, for the first time, it has become necessary to look to overseas sources to provide enough petroleum to meet projected needs. This increase in the demand for petroleum products occurs at a time when domestic reserves are capable of producing about 10,000,000 barrels of crude oil per day. In 1972, total consumption was of the order of 15,000,000 barrels per day.

Along with the need for increased imports, the recent clean fuel requirements have created a price differential system in the cost of imported oil as a function of its sulfur content. Nations which export oil have been quick to realize that low sulfur oil, which is in short supply, is much more valuable that high sulfur residual oils. Technology has been available in the past for producing low sulfur fuel oil from high sulfur residual oil, but this technology has heretofore been too expensive to apply on a large scale since there was no economic incentive for refiners to desulfurize high sulfur residuum oils.

Obviously, in the recent past, the situation has changed and the cost of desulfurization can be passed on to the consumer because of the short supply of low sulfur oil. It can be seen from Table 1, which was taken from the July 23, 1973 issue of Oil and Gas Journal (published weekly), that the cost of 0.3 percent sulfur fuel oil in the New York City market is about $5.50 per barrel. For fuel oil with 1.0 percent sulfur, the price is about $4.50 per barrel. The value of bunker C oil in the Caribbean is $2.40 per barrel. It is most interesting to note that the last figure of $2.40 per barrel for bunker C oil has not changed for at least two years. Comparable data is presented from a July 26, 1971 Oil and Gas Journal publication. The point of greatest interest is, of course, that the value of low sulfur oil has gone up sharply. There has been a difference of about $3.00 per barrel between the value of low sulfur oil at the point of consumption and high sulfur oil at the point of production. The cost of transporting oil from the Caribbean to the East Coast markets is on the order of $0.30 per barrel (at worldscale tanker rate of W100). It can therefore be seen that the

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Table 1. RESIDUAL FUEL OIL PRICES

(Source: Oil and Gas Journal)

	July 26, 1971 $/Bbl	July 23, 1973 $/Bbl
Mid Continent (Group 3)		
No. 6 (Less than 1% S)	2.60	2.60
No. 6 (1% S and Above)	2.50	2.50
Chicago		
No. 6 (Max 1% S)	4.62	5.57
No. 6 (Max. 1.25% S)	4.52	5.99
No. 5 (Max. 1% S)		
Gulf Coast (Cargoes)		
Bunker C Fuel (0.6% S)	3.70-3.80	4.15
Bunker C Fuel	3.00-3.25	
New York Harbor (Barges)		
No. 6 (Max. 1% S)	4.10	5.54-5.66
No. 6 (Max. 0.3% S)		4.59
No. 5 (Max. 1% S)		
California (Tank-Car-Truck)		
Bunker C Los Angeles Rack	3.60-3.70	3.70
Caribbean Area (Venezuelan Ports)		
Bunker C Fuel	2.41	2.35-2.40

price differential that one could apply to a processing operation is on the order of \$2.50-2.70 per barrel.

In the past, the major difficulty in desulfurizing high sulfur oil has been its tendency to poison catalysts by deposition of heavy metals, such as nickel and vanadium. An intermediate step to solving this problem was the construction in the late 1960's and early 1970's of very large heavy gas oil desulfurization units in the Caribbean. These units are capable of removing the heavy gas oil fraction, which normally contains only trace quantities of catalyst poisons, from the crude oil by vacuum distillation and desulfurizing it to 0.3 weight percent sulfur or less. This kind of operation is only a temporary solution since there is still a large amount of residual oil left for disposal. This material can be blended off with lower sulfur materials, such as desulfurized heavy gas oil, and marketed as fuel oil, which can be used as refinery fuel or for ships' bunkers. The latter two uses concentrate the use of high sulfur fractions in areas in which there are no sulfur emission specifications at the present time. However, this material is still quite valuable as a source of energy.

Technology had been developed earlier to remove the metals from the residual oil fraction so that the desulfurization catalyst, which is used in a subsequent operation, would not be rapidly poisoned. This technology is commercially viable, but is still relatively expensive because the demetallization removal reaction proceeds quite slowly over low cost, naturally occurring catalysts, which have been used for the demetallization step. It was the purpose of this work to develop materials which would allow much higher rates of metals removal from the petroleum residuum so the overall economics of desulfurization to environmentally acceptable levels would be improved.

The use of high pressure hydrogenation to desulfurize fuel oil is a capital intensive process. A significant portion of the capital required is devoted to the construction and installation of high pressure, large volume, continuous reactors. At the same time, the use of inactive demetallization agents to accomplish the demetallization requires that the residence time in these large reactors be lengthy. This results in unwanted consumption of hydrogen which is associated with the cracking of these residual oils, which does not of itself contribute to desulfurization. The use of a more active demetallization catalyst reduces costs in that it reduces capital requirements and improves hydrogen utilization, in that hydrogen is used for desulfurization rather than cracking. These improvements in cost must be weighed against the use of an improved demetallization catalyst which, of necessity, must cost more than the simple natural catalysts used previously.

SECTION IV

EXPERIMENTAL PROGRAM

LITERATURE SURVEY

A survey of U.S. Patents and other literature from 1954 to 1973 was made as the first step in the Experimental Program. The subject area was limited to the contacting of nickel- and vanadium-containing petroleum oils with solid catalysts or adsorbents at elevated temperatures and pressures under hydrogenation conditions. Furthermore, only literature which specifically referred to removal of these and/or other metallic contaminants (rather than general reference to metals laydown on catalysts with no specifics as to the nature of the contacting material or its demetallization capabilities) by contacting with solids as opposed to acid treating, etc., was considered. The bulk of the specific information on the subject was found in the patent literature. A list of the patents reviewed is presented in Table 2. Appendix A contains a detailed analysis of each patent.

Cited in the literature as petroleum demetallization catalysts were the oxides, sulfides, and other compounds of the Group V-B, Group VI-B, and Group VIII metals of the Periodic Table, unsupported or supported on a variety of solids. Most frequently cited as of potential interest were vanadium, chromium, molybdenum, tungsten, iron, cobalt, nickel, boron, manganese, and zinc. Others used in conjunction with solid supports were phosphorus compounds, such as phosphoric acid and titania. The demetallization superiority of one or more of these catalytic agents could not be gleaned from the literature.

Solids either employed as supports or containing no added catalytic agents are the refractory oxides alumina, silica, zirconia, magnesia, titania, and complexes of two or more of these oxides. Also cited were naturally occurring bauxites and clays, as well as solid carbons. Most frequently mentioned and employed in examples in patents were alumina, silica alumina, bauxites, clays, and solid carbons. Price considerations would also tend to single out many of this latter group.

Table 2. PETROLEUM DEMETALLIZATION CATALYSTS

BIBLIOGRAPHY OF U.S. PATENTS 1954-1973

U.S. Patent Number	Inventor(s)	Year of Issue
3,725,251	S. B. Alpert et al	1973
3,716,479	P. B. Weisz and A. J. Silvestri	1973
3,712,861	E. J. Rosinski and F. A. Smith	1973
3,696,027	A. G. Bridge	1972
3,691,063	M. C. Kirk, Jr.	1972
3,617,481	A. Voorhies and G. P. Hammer	1971
3,607,725	R. L. Irving	1971
3,576,737	D. S. Mitchell	1971
3,563,887	M. D. Frazier et al	1971
3,553,106	H. A. Hamilton et al	1971
3,530,066	T. Kuwata et al	1970
3,383,301	H. Beuther and B. K. Schmid	1968
3,362,901	S. L. Szeke et al	1968
3,297,589	W. K. T. Gleim	1967
3,227,645	H. A. Frumkin et al	1966
3,180,820	W. K. T. Gleim et al	1965
2,987,470	M. Turken	1961
2,970,957	R. P. Northcrott et al	1961
2,945,803	H. Beuther et al	1960
2,891,005	R. L. Heinrich	1959
2,891,004	W. J. Mattox	1959
2,769,758	F. W. B. Porter et al	1956
2,764,525	F. W. B. Porter et al	1956
2,730,487	F. W. B. Porter et al	1956
2,687,985	F. W. B. Porter et al	1954

Most of the literature published in recent years stresses the need for extensive macroporosity (even at the expense of high internal surface area) to allow access of the high molecular weight metal-containing species into the catalyst and prevent pore plugging or deactivation of the demetallization catalyst. This macroporosity is defined variously as pores of average diameter greater than a few hundred angstroms to a plurality of pores of diameters between 1,000 and 50,000 angstroms (i.e. 0.1 to 5.0 microns).

DEMETALLIZATION CATALYST PREPARATION

In order to meet the requirements of developing an improved, yet low cost, demetallization catalyst only compounds of iron, cobalt, vanadium, nickel, chromium, and molybdenum of the potential metals in Groups V-B, VI-B, and VIII of the Periodic Table were employed in the preparation of the catalysts described in the following pages. The other metals in these Groups, such as platinum and palladium, for example, were considered too expensive to be employed in a low cost, "throw-away" type of demetallization catalyst.

Although a number of catalyst preparation methods, such as coprecipitation of promoter metal and support material, impregnation of specially prepared supports, or the incorporation of one type of support material in a matrix of a different type of support material, were cited in the literature, these methods would not allow the resulting catalysts to be available at a maximum $0.25 per pound. This limiting price was based on our calculations which indicated that the catalyst would probably have twice the activity (and the same bulk density) of the lowest cost, unpromoted activated bauxite demetallization catalyst known to us. For this reason, the promoter metals were incorporated into the support materials using a simple solution impregnation followed by drying and air calcination.

Although a wide variety of support materials were cited in the literature, many of these were either not readily available for use in the program, judged as not having a sufficiently open pore structure for use with the heavy vacuum residua used in this program, or else too costly to meet the requirements of a low cost catalyst. Since the development of specialized support materials is beyond the scope of this program, the supports used were chosen on the basis of their ready commercial availability, low or moderate cost, or as "model type" porous structures that would provide guidance for the choice of a commercially available support material.

Table 3 summarizes data on the six types of support materials used in this study. Although these materials came in different sizes, all, except supports 3 and 4, were crushed and sieved to either 12 x 20 mesh or 20 x 50 mesh. In the case of support 3 (the activated clay), which came in 16 x 30 mesh granules, crushing to 20 x 50 mesh was required for some preparations. Support 4 (the activated bauxite) came from the supplier in both 10 x 20 mesh (HRI 2765) and 20 x 60 mesh (HRI 3309) sizes and only had to be sieved to remove the oversize in the former and the undersize in the latter.

Pore volume distribution curves, as obtained using a 60,000 psia AMINCO (American Instrument Company, Silver Springs, Maryland) mercury porosimeter, for the six supports are presented in Figure 1. This technique is based on filling the catalyst pores with mercury by continuously increasing the applied pressure. The pressure required to fill the pores of a specific size is mathematically related to the size of the pores. The upper and lower absissa scales provide the equivalent values of the pressure and pore diameter.

In order to compare the pore volume distributions on a common basis, the specific pore volumes (cc/g) in pores above a given diameter were multiplied by the compacted bulk densities given in Table 3 (cc/g) yielding curves of cumulative pore volume per volume of packed catalyst (cc/cc) versus pore diameter. Since all but one of the packed densities were determined on the same size material (12 x 20 mesh), the assumption of uniform particle packing is felt to be a reasonable approximation. Furthermore, the distribution curves for both the 12 x 20 mesh and 20 x 50 mesh materials represented by support 4 (the activated bauxite) could be superimposed one upon the other and therefore appear as a single curve.

As shown in Figure 1, the pore size distributions of these supports range from very macroporous, monodisperse systems (support 5) to bidisperse systems with a broad distribution in both macro- and micropores (support 4). Although not shown in the figure, the high surface area activated carbon has a significant volume in pores less than about 25 angstroms (0.025 microns) in diameter.

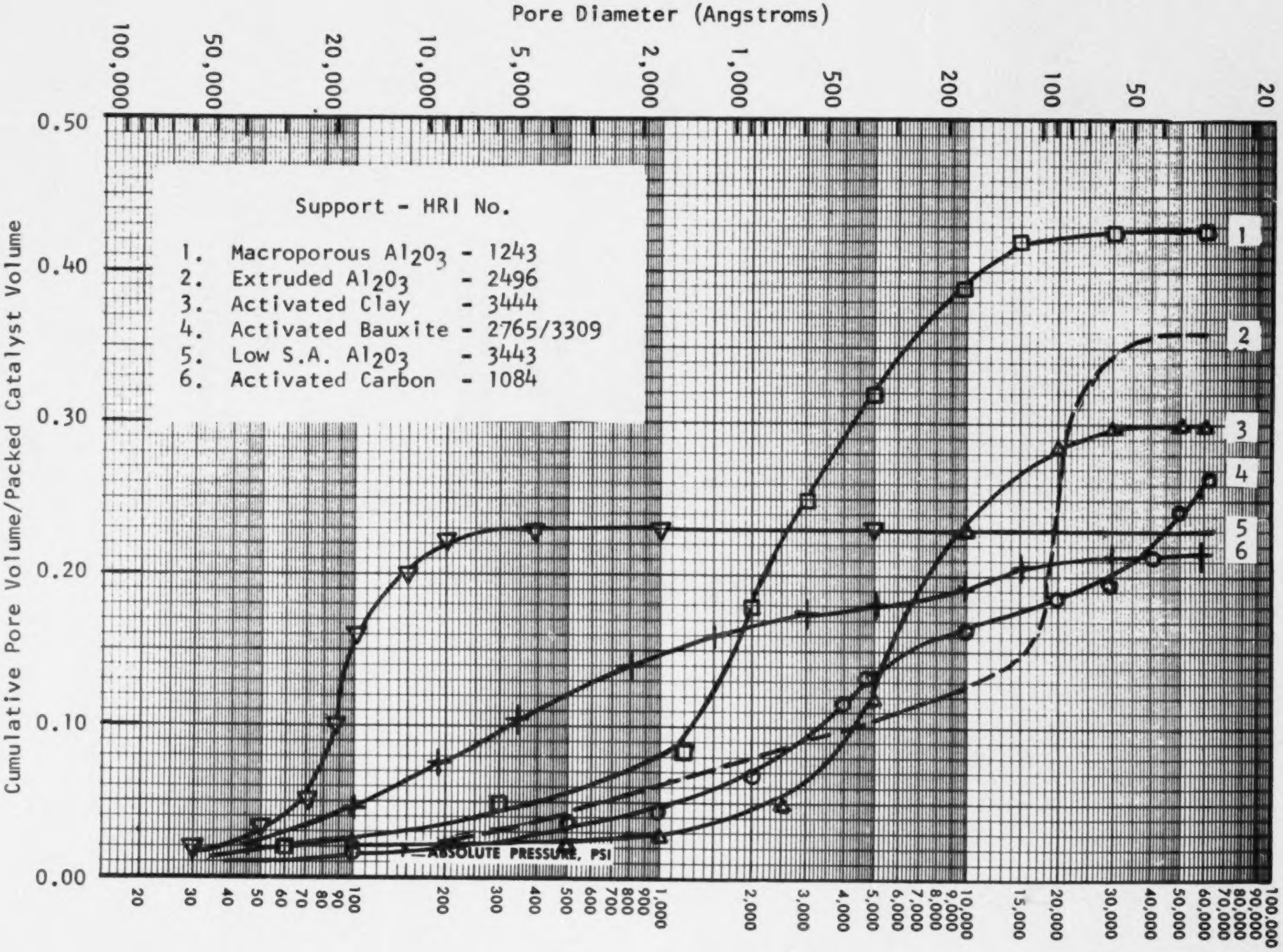
Table 3. CATALYST SUPPORTS

Support No.[a] HRI No.	Description[b]	Compacted Bulk Density, g/cc
1-1243	Norton Intermediate Surface Area (35 M^2/g) Macroporous Alumina	0.83
2-2496	Cyanamid Unpromoted Alumina Extrudates (Surface Area 270 M^2/g)	0.55
3-3444	Engelhard LVM Attasorb® Activated Attapulgus Clay (Surface Area 125 M^2/g)	0.52
4-2765/3309	Engelhard Regular Iron 2% V.M. Porocel® Activated Bauxite (Surface Area $\sim$175 M^2/g)	0.98/1.04
5-3443	Norton Low Surface Area (<1 M^2/g) Type LA956 Alumina	1.35
6-1084	Pittsburgh Activated Carbon Type CAL (Surface Area 1000-1100 M^2/g)	0.44

a. Refers to Support No. in Figure 1.

b. Although "as received" supports were of various sizes, either 12 x 20 mesh or 20 x 50 mesh sizes were used in the preparation of demetallization catalysts.

Figure 1. PORE VOLUME DISTRIBUTION OF DEMETALLIZATION CATALYST SUPPORTS



Generalized Demetallization Catalyst Preparation Procedure

A total of twenty-seven different demetallization catalysts were prepared. Table 4 lists the code number, impregnant, porous support, and the compounds used in the preparation of the catalysts.

In nearly all cases, the supports were air calcined at 950°F for a minimum of four hours prior to impregnation from solution. The starting compounds were dissolved in water except where indicated in the table. Impregnation was accomplished by contacting the support with just enough liquid to cover and evaporating slowly to dryness. A final 950°F air calcination was made to decompose the impregnating salts and convert the metals to their oxides. One exception was the air calcination of LX-16 at 650°F. This was done to prevent the gasification of the activated carbon support. Although titanium and its compounds supported on porous solids were mentioned earlier in this report, no titanium catalyst was prepared due to problems encountered in the preparation chemistry.

Detailed preparation procedures for each catalyst are given in Appendix B.

APPARATUS AND PROCEDURE

Using the demetallization catalysts that were prepared, short term demetallization runs were carried out using a single petroleum residuum for the purpose of determining the effectiveness of these materials. The feed chosen for the screening runs was Tia Juana vacuum residuum, a high vanadium and nickel content Venezuelan residuum. Nominal inspections on this feed are 2.8 weight percent sulfur, 550 ppm vanadium, 74 ppm nickel, and 7.0°API gravity. This residuum consists mainly of that fraction of crude which boils above 975°F.

All screening runs were carried out in continuous, downflow, fixed bed reactor systems. A schematic diagram is shown in Figure 2. The reactor, fabricated of 1-1/2-inch O.D. by 1-inch I.D. stainless steel tubing, has a catalyst bed length of approximately 16 inches. A drawing of the reactor tube is shown in Figure 3. The volume (loose) of catalyst charged to the reactor was 200 cc. Provision was made for an internal thermocouple which is positioned in the center of the catalyst bed approximately

Table 4. DEMETALLIZATION CATALYSTS

Code Number	Impregnant	Support Solid	Starting Compounds
LX-1	5.0 W % as Fe	12 x 20 Mesh Activated Bauxite (HRI 2765)	$Fe(NO_3)_3$ $9H_2O$
LX-2	5.0 W % as Co	12 x 20 Mesh Activated Bauxite (HRI 2765)	$Co(NO_3)_2$ $6H_2O$
LX-3[a]	5.0 W % as V	12 x 20 Mesh Activated Bauxite (HRI 2765)	NH_4VO_3, NaOH
LX-4	5.0 W % as Mo	12 x 20 Mesh Activated Bauxite (HRI 2765)	MoO_3, NH_4OH
LX-5	5.0 W % as V	12 x 20 Mesh Activated Bauxite (HRI 2765)	V_2O_5, Oxalic Acid
LX-6	5.0 W % as (HPO_3)	12 x 20 Mesh Activated Bauxite (HRI 2765)	H_3PO_4
LX-7	7.6 W % as Ni	12 x 20 Mesh Activated Bauxite (HRI 2765)	$Ni(NO_3)_2$ $6H_2O$
LX-8	5.0 W % as C_R	12 x 20 Mesh Activated Bauxite (HRI 2765)	$C_R(NO_3)_3$ $9H_2O$
LX-9	10.0 W % as Fe	12 x 20 Mesh Activated Bauxite (HRI 2765)	$Fe(NO_3)_3$ $9H_2O$
LX-10	10.0 W % as V	12 x 20 Mesh Activated Bauxite (HRI 2765)	V_2O_5, Oxalic Acid
LX-11	5.0 W % as Fe	12 x 20 Mesh Low SiO_2 Activated Bauxite (HRI 2753)	$Fe(NO_3)_3$ $9H_2O$
LX-12	5.0 W % as Fe	12 x 20 Mesh Macroporous Alumina (HRI 1243)	$Fe(NO_3)_3$ $9H_2O$
LX-13	1.5 W % as Co 5.0 W % as Mo	12 x 20 Mesh Activated Bauxite (HRI 2765)	$Co(NO_3)_2$ $6H_2O$ MoO_3, NH_4OH
LX-14	5.0 W % as Mo	12 x 20 Mesh Macroporous Al_2O_3 (HRI 1243)	MoO_3, NH_4OH

a. No screening runs were made using these catalysts.

Table 4 (continued). DEMETALLIZATION CATALYSTS

Code Number	Impregnant	Support Solid	Starting Compounds
LX-15	9.5 W % as Mo	12 x 20 Mesh Attapulgus Clay (HRI 3444)	MoO_3, NH_4OH
LX-16	11.0 W % as Mo	12 x 20 Mesh CAL Activated Carbon (HRI 1084)	MoO_3, NH_4OH
LX-17	3.8 W % as Mo	12 x 20 Mesh Low Surface Area Al_2O_3 (HRI 3443)	MoO_3, NH_4OH
LX-18	2.0 W % as Mo	12 x 20 Mesh Activated Bauxite (HRI 2765)	MoO_3, NH_4OH
LX-19	8.9 W % as Mo	1/16" High Porosity Extruded Al_2O_3 (HRI 2496)	MoO_3, NH_4OH
LX-20	2.0 W % as Mo	12 x 20 Mesh Activated Attapulgus Clay (HRI 3444)	MoO_3, NH_4OH
LX-21	1.0 W % as Mo	12 x 20 Mesh Activated Bauxite (HRI 2765)	MoO_3, NH_4OH
LX-22[b]	2.0 W % as Mo	20 x 50 Mesh Activated Bauxite (HRI 3309)	MoO_3, NH_4OH
LX-23	0.5 W % as Mo	12 x 20 Mesh Activated Bauxite (HRI 3309)	MoO_3, NH_4OH
LX-24	1.0 W % as Zn	12 x 20 Mesh Activated Bauxite (HRI 3309)	MoO_3, NH_4OH
LX-25[a]	0.3 W % as Ni 1.0 W % as Mo	12 x 20 Mesh Activated Bauxite (HRI 3309)	$Ni(NO_3)_2\ 6H_2O$ MoO_3, NH_4OH
LX-26	0.5 W % as Mo	20 x 50 Mesh Activated Bauxite (HRI 3309)	MoO_3, NH_4OH
LX-27	1.0 W % as Mn	20 x 50 Mesh Activated Bauxite (HRI 3309)	$Mn(NO_3)_2\ 6H_2O$

a. No screening runs were made using these catalysts.

b. Five different preparations (LX-22-1, -2, -3, -4, and -5) of this catalyst were made for use in various demetallization operations.

Figure 2. FIXED BED DEMETALLIZATION UNIT

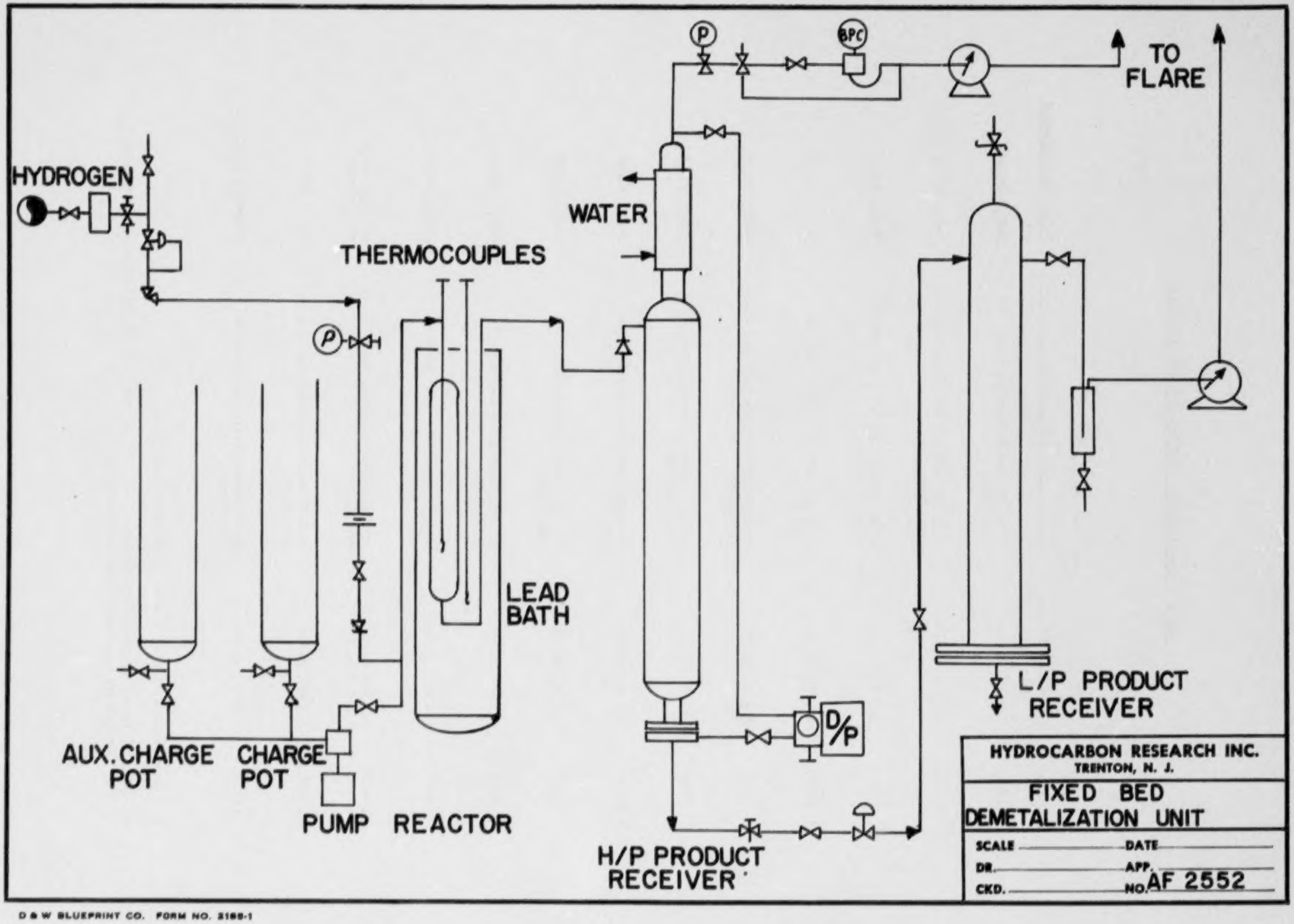
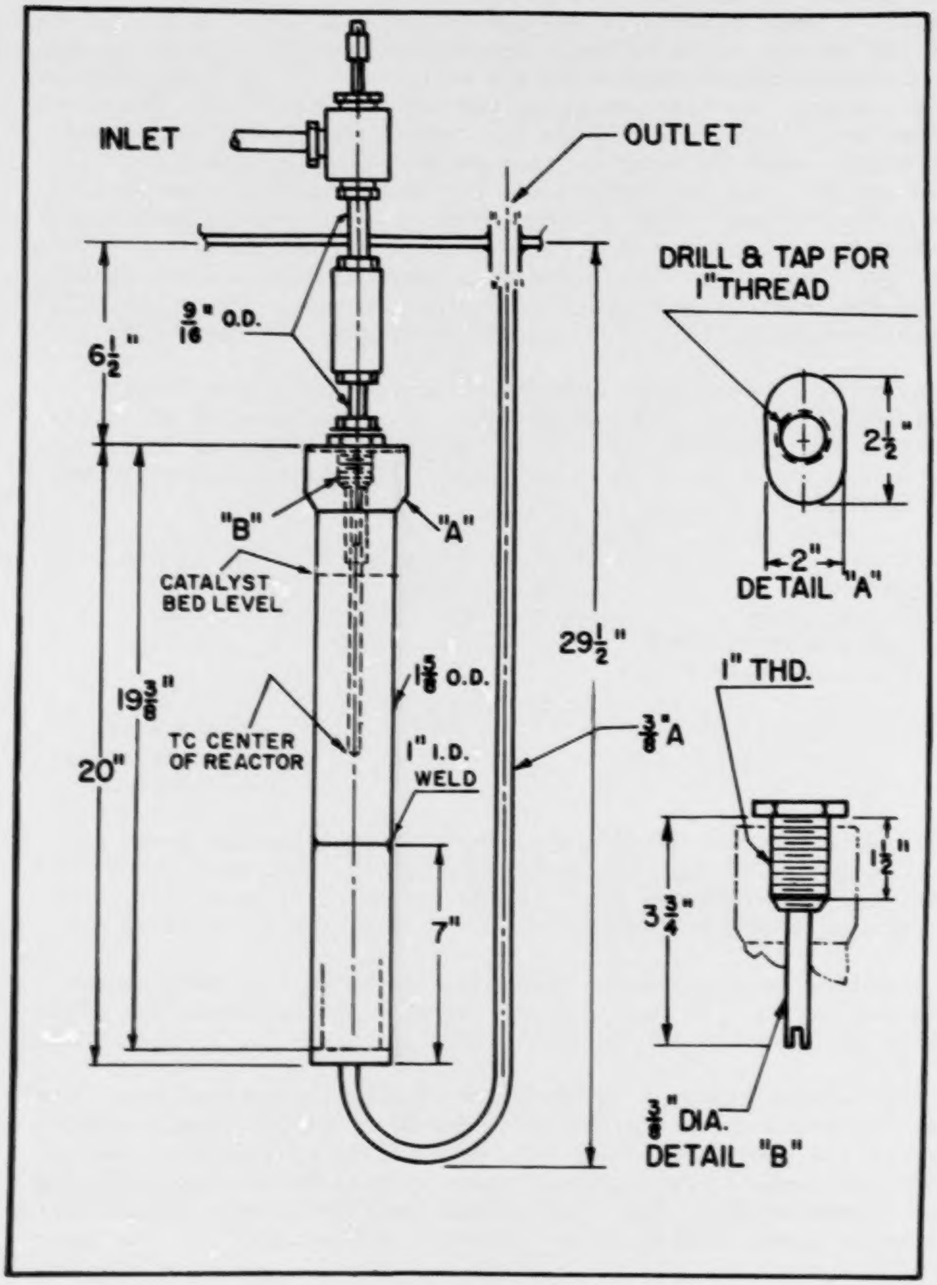

HYDROGEN
P
THERMOCOUPLES
LEAD BATH
AUX. CHARGE POT
CHARGE POT
PUMP
REACTOR
WATER
P
BPC
TO FLARE
D/P
H/P PRODUCT RECEIVER
L/P PRODUCT RECEIVER
HYDROCARBON RESEARCH INC.
TRENTON, N. J.
FIXED BED DEMETALIZATION UNIT
SCALE
DATE
DR.
APP.
CKD.
NO. AF 2552
D & W BLUEPRINT CO. FORM NO. 2188-1

Figure 3. FIXED BED DEMETALLIZATION REACTOR



INLET
OUTLET
DRILL & TAP FOR 1" THREAD
$\frac{9}{16}$" O.D.
$6\frac{1}{2}$"
$2\frac{1}{2}$"
"B"
"A"
2"
DETAIL "A"
CATALYST BED LEVEL
$29\frac{1}{2}$"
$1\frac{5}{8}$ O.D.
1" THD.
$19\frac{3}{8}$"
TC CENTER OF REACTOR
$\frac{3}{8}$"A
20"
1" I.D.
WELD
$1\frac{1}{2}$"
$3\frac{3}{4}$"
7"
$\frac{3}{8}$" DIA.
DETAIL "B"

midway between the top and bottom. Heat to the reactor was supplied by a lead bath.

The melted charge stock was pumped to reactor pressure with a metering pump, mixed with hydrogen makeup gas, and fed to the top of the reactor. The hydrogen concentration of the makeup gas was 100 percent and no recycle of the exit gases was employed. In the reactor, the feed was contacted with the catalyst. The mixed vapor and liquid product from the reactor was cooled and passed to a high pressure receiver from which gas was sampled, metered, and vented. The net product was let down in pressure and passed to a low pressure receiver from which gas was sampled periodically, metered, and vented. The liquid product was collected and weighed periodically. Upon completion of a run, the catalyst was removed from the reactor for inspection and/or analyses. Three essentially identical units, 184, 185, and 201, were used for these runs.

A standard procedure was devised to screen the demetallization catalysts in short term operations. This consisted of an initial startup period which conditioned the fresh catalyst at lower temperatures for a short period of time. This startup schedule was as follows:

Period	------- 1A -------			1B, 2, etc.
Temperature, °F	750	775	790	790
Pressure, psig	2000	2000	2000	2000
Hydrogen Rate, SCF/Bbl	4000	4000	4000	4000
Liquid Space Velocity, $V_o/hr/V_r$	0.75	0.75	0.50	0.50
Time on Temp., Hrs.	4	4	1	Continue at above conditions until shutdown.

After the unit was lined out at 790°F, the period was ended and the remainder of the run continued at 790°F, 2000 psig, 4000 SCF/Bbl, and 0.50 $V_o/hr/V_r$ for a period of two to fifteen days, depending upon the performance of the catalyst being screened.

A standard demetallization screening run using Tia Juana vacuum bottoms and 12 x 20 mesh Porocel was made at the conditions cited above to establish a reference point.

A preliminary study of the kinetics of vanadium removal over Porocel indicated that simple first order kinetics are adequate to describe the rate of vanadium (the major metal contaminant) removal over the range of variation in space velocities that occur during the screening run. The kinetic equation used to correct for variations in space velocities and obtain rate constants for use later in this program is given in Equation (1).

$$\ln V_F/V_P = K_M\left(\frac{1}{C.S.V.}\right) \qquad (1)$$

CATALYST SCREENING TEST RESULTS

A summary of the 33 screening runs that were made with either impregnated supports (29 runs) or the supports themselves is presented in Table 5. Each of the catalysts prepared is identified by an LX number and will be referred to by that number for convenience.

The demetallization and desulfurization levels were essentially constant for the duration of some of the screening runs and average values to the nearest five percent are cited in these cases. However, when there was a significant decrease in either demetallization or desulfurization with age, the initial and final levels are given along with the run duration. More complete operating data on these screening runs are given in Appendix C.

In order to simplify discussion of the screening tests, the runs are grouped in such a way that some common objectives and conclusions can be made for each grouping.

Group A - Promoter Metals: LX-1 through -10, -13, -24, and -27

Before attempting to test other support materials, 12 x 20 mesh activated bauxite was impregnated with six metals (Fe, Co, Mo, Cr, V, and Ni) and one nonmetal (phosphoric acid) at the five percent level, to test the effect that these promoters would have in improving demetallization activity. The effect of concentration was studied by looking at 10 percent V (LX-9) and 10 percent Fe (LX-10) levels. Later in the program, a combination of 1.5 percent Co together with five percent Mo (LX-13), one percent Zn (LX-24) and one percent Mn (LX-27) were evaluated.

Conclusions drawn from these screening runs were:

1. Although impregnation of the 12 x 20 mesh activated bauxite with these known hydrogenation catalysts resulted in as much as a 30 percent improvement in vanadium removal and

Table 5. SUMMARY OF DEMETALLIZATION CATALYST SCREENING OPERATIONS USING TIA JUANA VACUUM RESIDUUM

Run	Catalyst[a]	% Metals Removal		% Desulfurization	Run Duration, Days
		V	Ni		
185-192	Activated Bauxite, HRI 2765 (Standard Catalyst)	50	20	20	9
185-157	5% Fe/Activated Bauxite, LX-1	62	20	20	8
185-193	5% Co/Activated Bauxite, LX-2	55	15	20	4
185-194	5% Mo/Activated Bauxite, LX-4	65	45	60	3
184-158	5% V/Activated Bauxite, LX-5	60	25	20	4
185-195	5% (HPO_3)/Activated Bauxite, LX-6	48	10	10	3
184-159	7.5% Ni/Activated Bauxite, LX-7	60	20	20	3
185-196	5% C_R/Activated Bauxite, LX-8	65-50	20	15	3
184-160	10% Fe/Activated Bauxite, LX-9	63	35	20	4
185-197	10% V/Activated Bauxite, LX-10	70-60	40-30	25	3
184-161	5% Fe/Low SiO_2 Activated Bauxite, LX-11	58	20	20	3
185-198	5% Fe/Macroporous Alumina, LX-12	(Involuntary shutdown due to pump malfunction)			1
185-199	Activated Attapulgus Clay, HRI 3444	55	20	20	7
184-164	5% Fe/Macroporous Al_2O_3-1243, LX-12	50	10	15	2
184-162	1.5% Co + 5% Mo/Activated Bauxite, LX-13	70-65	45-40	60	6
184-163	5% Mo/Macroporous Al_2O_3-1243, LX-14	70-60	25-10	35-30	4

a. All support materials are 12 x 20 mesh unless otherwise indicated.

Table 5 (continued). SUMMARY OF DEMETALLIZATION CATALYST SCREENING OPERATIONS USING TIA JUANA VACUUM RESIDUUM

Run	Catalyst[a]	% Metals Removal		% Desulfurization	Run Duration, Days
		V	Ni		
185-200	9.5% Mo/Activated Attapulgus Clay, LX-15	70-60	45-20	35-25	4
185-201	11% Mo/Activated Carbon 1084, LX-16	60	35	40	3
185-202	3.8% Mo/Low Surface Area, Al_2O_3-3443, LX-17	20	Nil	10	2
184-165	2% Mo/Activated Bauxite, LX-18	65-60	35	50	11
185-203	8.9% Mo/High Porosity Extruded Al_2O_3-2496, LX-19	60	40	50	3
185-204	2% Mo/Activated Attapulgus Clay, LX-20	70-55	40-25	35-25	6
185-205	1% Mo/Activated Bauxite, LX-21	70-65	40-30	50	7
184-166	2% Mo/20 x 50 Mesh Activated Bauxite, LX-22-1	80-75	45-40	60	7
185-207	LX-22-1 (At 1000 psig hydrogen pressure)	75-50	25	40	3
185-211[b]	2% Mo/20 x 50 Mesh Activated Bauxite, LX-22-3	80-70	55-40	60	7
185-206	0.5% Mo/Activated Bauxite, LX-23	65	35	40	5
184-167	20 x 50 Mesh Activated Bauxite, HRI 3309	55	15	10	3
185-208	30 x 60 Mesh Activated Attapulgus Clay, HRI 3310	70-60	40-25	25	5
185-168	1% Zn/Activated Bauxite, LX-24	55	5	20	3
184-169	0.5% Mo/20 x 50 Mesh Activated Bauxite, LX-26	75	35	40	6
184-171	1% Mn/20 x 50 Mesh Activated Bauxite, LX-27	65	30	25	3

a. All support materials are 12 x 20 mesh unless otherwise indicated.

b. Run to confirm the results obtained in Run 184-166 with a different preparation of the 2% Mo/20 x 50 mesh activated bauxite catalyst.

150 percent improvement in nickel removal (in the case of 5% molybdenum on the activated bauxite) for a short term operation, none of the catalysts prepared offered the improvement in activity (approximately 75% metals removal at the standard conditions) which was sought.

2. The lack of response to increases in the level of catalytic impregnants, 10 percent Fe (LX-9) versus five percent Fe (LX-1), and/or the rapid loss in activity when the level of impregnant is increased, 10 percent V (LX-10) compared to five percent V (LX-5), indicated that an improvement in the demetallization activity may be limited by the limited macroporosity of the standard activated bauxite support or the high SiO_2 content of the bauxite promoted cracking and subsequent deactivation due to coke laydown.

3. The impregnation of molybdenum, while offering essentially the same or slightly more improvement in demetallization, also was much more selective for the simultaneous removal of sulfur and nickel than any of the other promoters.

Group B - Supports: LX-11, -12, -14, -15, -16, -17, -19 and Activated Clay

Several other supports were evaluated to determine if the type of support and/or porous structure might enable a higher demetallization activity to be obtained either through better access of the metal-containing species to the promoter metal in the catalyst pores or by the prevention of rapid catalyst deactivation by pore blockage with either metals or coke. When using supports having a different density than Porocel, the standard catalyst, the weight percent metals were adjusted so that the amount of the catalytic element charged to the reactor was equal to that corresponding to an impregnated Porocel. In this way, the effect of pore structure rather than amount of catalytic impregnant was studied.

The conclusions of this set of runs were:

1. When five percent iron was added to the low SiO_2 Porocel (LX-11), vanadium removal was somewhat lower than five percent iron on regular Porocel. Since the low SiO_2 Porocel only had 1.5 percent iron as Fe_2O_3 compared to about 12 percent iron as Fe_2O_3 on regular Porocel, it

may be that the iron content of the activated bauxite itself may be catalyzing the demetallization reaction. Because of this effect, it is not possible to determine if the lower SiO_2 content reduced cracking and subsequent pore blockage.

2. Although a certain amount of macroporosity is required to enable the large metal-containing asphaltene species to gain entry into the catalyst, a broad distribution of both macropores (broadly defined as pores with a pore diameter greater than 100 Å) and micropores (again, broadly defined as pores having a diameter less than about 100 Å) are needed for both high demetallization activity, both vanadium and nickel removal, and the maintenance of this activity. The activated bauxite appears to be the best compromise between having the required type of overall pore size distribution and low cost. Unimpregnated activated Attapulgus clay was about equal to or slightly better than the unimpregnated bauxite. However, the molybdenum impregnated clay (LX-15) deactivated at a significantly higher rate than did the molybdenum impregnated bauxite. It is believed that the more "narrow" pore size distribution of the clay (Curve 3, Figure 1) compared to the bauxite results in a greater rate of deactivation due to pore blockage by the deposited metals and "coke". Demetallization activity ranged from poor for the low surface area alumina (LX-17, Curve 5) to a level approximating that of the activated bauxite (Curve 4) for the activated carbon (LX-16) and the other aluminas (Curves 1 and 3, LX-14 and LX-19, respectively). The impregnation of molybdenum onto an alumina support having the broad size distribution characteristic of a commercial porous type hydrodesulfurization catalyst (LX-19) did not produce the improvement in demetallization expected of this "model" support. This suggests that perhaps there are definite limitations on the level to which Tia Juana vacuum bottoms can be demetallized at the standard screening conditions. Since these other supports are more costly than the $0.05 per pound activated bauxite, they offer no advantage.

3. The Tia Juana vacuum residuum is a very difficult feed to demetallize. This is thought to be due in part to the fact that it is a very "heavy" residuum and mass transport of the higher molecular weight, metals-containing species into the interior of the 12 x 20 mesh (~ 1.8 mm diameter) granules may limit the effective

demetallization activity of the impregnated supports and result in a low catalyst effectiveness factor. This suggested that a reduction in particle size might improve the situation.

Group C - Promoter Levels and Particle Size: LX-18, -20, -21,-22, and -23

In order to try to meet the objective of keeping the cost of the demetallization catalyst to a minimum, the effect of lower levels of molybdenum promoter were investigated. Samples containing 2.0 (LX-20), 1.0 (LX-21), and 0.5 (LX-22) percent showed that neither the initial demetallization activity nor the rate of deactivation (up to five days) were significantly different for these samples compared to each other. When the level of molybdenum on Porocel is reduced from five percent to two percent (LX-18), there is no difference in the level of vanadium removal (65%), but some reduction in the levels of nickel (45% down to 35%) and sulfur (60% down to 50%). Therefore, it appears very low levels of Mo are capable of catalyzing demetallization by Porocel. This is an important cost consideration. However, some question remains about the aging rate as a function of the promoter level.

By reducing the size of the Porocel support from 12 x 20 mesh to 20 x 50 mesh for preparation LX-22 containing two percent molybdenum, it was possible to attain initial vanadium removal levels in excess of 75 percent. Operations of seven days indicated only a slight activity decline. However, when the hydrogen pressure was reduced from 2000 psig to 1000 psig in an attempt to determine if satisfactory operation could be achieved at a lower pressure, a rapid decline in vanadium removal activity occurred. This was probably due to rapid coking occurring in the catalyst pores resulting from low pressure operations, since the initial level (75%) is just slightly under the initial level (80%) for the 2000 psig operation. Higher Mo levels, for example five percent, might provide the hydrogenation activity to limit coking at 1000 psig, but would add considerably to the cost (~ $0.02/percent Mo) of a cheap demetallization catalyst.

In order to determine the effect of particle size on demetallization, 20 x 50 mesh activated bauxite was investigated. Reduction of the size to 20 x 50 mesh resulted in a somewhat higher vanadium removal activity. However, it was lower than the Mo impregnated 12 x 20 mesh Porocel and substantially lower than the Mo impregnated 20 x 50 mesh Porocel.

Although the two percent Mo/activated Attapulgus clay (LX-20) had initial demetallization and desulfurization activities of the 9.5 percent Mo/activated clay, this catalyst suffered a rapid deactivation compared to the two percent Mo/Porocel. Although the clay support offers a definite cost advantage (\$0.02/pound versus \$0.04/pound for Porocel), Porocel appears to be a better support, possibly because of its more broad pore size distribution. Evaluation of unpromoted 30 x 60 mesh Attapulgus clay indicated the same rapid decline in demetallization activity noted with the other clay preparations.

Results of Screening Program

As a result of the screening program, activated bauxite impregnated with small amounts of molybdenum was found to be the best overall demetallization catalyst system on the basis of both high demetallization activity (i.e., the rates of nickel and vanadium removal achieved) and the maintenance of this high activity when used for the demetallization of heavy vacuum residua. An added plus for this catalyst system is its moderately high desulfurization activity considering its low Mo loading. The effects of molybdenum loading and particle size for the molybdenum/activated bauxite catalyst system is shown in Table 6. The rate of metals removal does not appear to be a strong function of the level of molybdenum loading on a given sized support. Although a significant increase in demetallization activity over the unpromoted bauxite is found for the larger 12 x 20 mesh (0.066" to 0.033") catalyst, only a reduction in particle size, to 20 x 50 mesh (0.033" to 0.012"), allows the attainment of the 75-80 percent vanadium removal rate that has been the goal of this program.

In kinetic terms*, the rate constant for vanadium removal for the two percent Mo/20 x 50 mesh activated bauxite catalyst is approximately twice that of the unpromoted activated bauxite. The superior performance of the smaller 20 x 50 mesh catalyst is thought to be due to the greater accessibility of the molybdenum impregnant to the high molecular weight metals-containing components known to be in heavy vacuum residua such as Tia Juana. Since the other vacuum residua chosen for demetallization also contain high

* The rate of vanadium removal is approximately first order in vanadium concentrations over the range of vanadium removal studied.

Table 6. SUMMARY OF DEMETALLIZATION CATALYST SCREENING DATA

	Percent Metals Removal at Standard Conditions							
Mo Loading (W %)	2.0		1.0		0.5		0	
	V	Ni	V	Ni	V	Ni	V	Ni
Support/Mesh Size								
Activated Bauxite/12 x 20	65-60	35	70-65	40-30	65	35	50	20
Activated Bauxite/20 x 50	80-75	40	-----	-----	75	35	55	15

molecular weight metal-containing species, the two percent Mo/20 x 50 mesh activated bauxite catalyst, referred to from this point on as the LX-22 series catalyst, was chosen for the preparation of demetallized feeds discussed in the following section. Although the short term screening runs indicate the 0.5 percent Mo/20 x 50 mesh activated bauxite has nearly the same activity, the scope of this program is not such that the optimization of Mo loading could be studied in the subsequent demetallization runs which followed.

DETAILED ANALYSES OF LX-22: TWO PERCENT MOLYBDENUM ON 20 x 50 MESH ACTIVATED BAUXITE

The activated bauxite used for the preparation of the LX-22 catalyst was obtained from Minerals and Chemicals Division of Engelhard, Inc., and is commercially known as Porocel. Analyses of this material are given in Table 7. Atomic absorption spectrophotometry was used to measure the molybdenum concentration on the various LX-22 preparations that were used in the screening work, as well as in subsequent preparations made for the long term demetallization feed production runs. These data are summarized in Table 8. All the other metal analyses previously given in Table 5 were calculated from the amount of impregnating solution absorbed during catalyst preparation. This approach was necessary since lamps for many of the other elements were not on hand for the spectrophotometer and it was not deemed necessary to purchase them.

Pore volume distribution curves for 20 x 50 mesh Porocel support, LX-22 blank preparation, and a typical LX-22 impregnated demetallization catalyst support are presented in Figure 4. These show that treatment of the support with NH_4OH, followed by drying and air calcination, develops additional porosity over the support. Possible mechanisms include (a) leaching of soluble mineral or (b) structural rearrangement upon dehydration of the minerals in the activated bauxite. Although some differences are indicated in the pore size distribution in Figure 5, they are not considered significant.

Figure 6 presents pictures of the scanning electron microscope studies done on LX-22-1, along with X-Ray mappings of the location of Al and Mo on the finished catalyst. The catalyst samples were prepared by embedding the particles in an epoxy resin. After hardening, the solid mass was partially immersed in liquid nitrogen. This resulted in the fracture of the granular particles

Table 7. DESCRIPTION AND ANALYSES[a] OF THE ACTIVATED BAUXITE SUPPORT USED IN THE PREPARATION OF THE LX-22 CATALYSTS

Supplier	Engelhard Minerals & Chemicals Corporation Menlo Park Edison, New Jersey 08817
Grade	Regular Porocel®
Volatile Matter, W % (Weight Loss at 1800°F)	2
Size (As Received)	20 x 60 U.S. Mesh
Chemical Composition (Volatile Free Basis)	
Al_2O_3, W %	78.0
Fe_2O_3, W %	8.0
TiO_2, W %	4.0
SiO_2, W %	9.0
Insolubles, W %	1.0
Surface Area, M^2/g	175
Bulk Density, g/cc	0.90

a. Analyses furnished by supplier (nominal values) from Technical Information Report No. 1004

Table 8. MOLYBDENUM CONTENT AND COMPACTED BULK DENSITY OF VARIOUS LX-22 PREPARATIONS

	W % Mo	Compacted Bulk Density g/cc
LX-22-1	2.09	0.97
LX-22-2	2.40	1.00
LX-22-3	2.27	0.97
LX-22-4	2.17	1.02
LX-22-5	2.24	1.04
LX-22 Blank	0.0	1.07
HRI 3309 (20 x 50 Mesh Porocel)	0.0	1.04

Figure 4. ALTERATION OF THE PORE VOLUME DISTRIBUTION OF ACTIVATED BAUXITE DURING IMPREGNATION WITH MOLYBDENUM

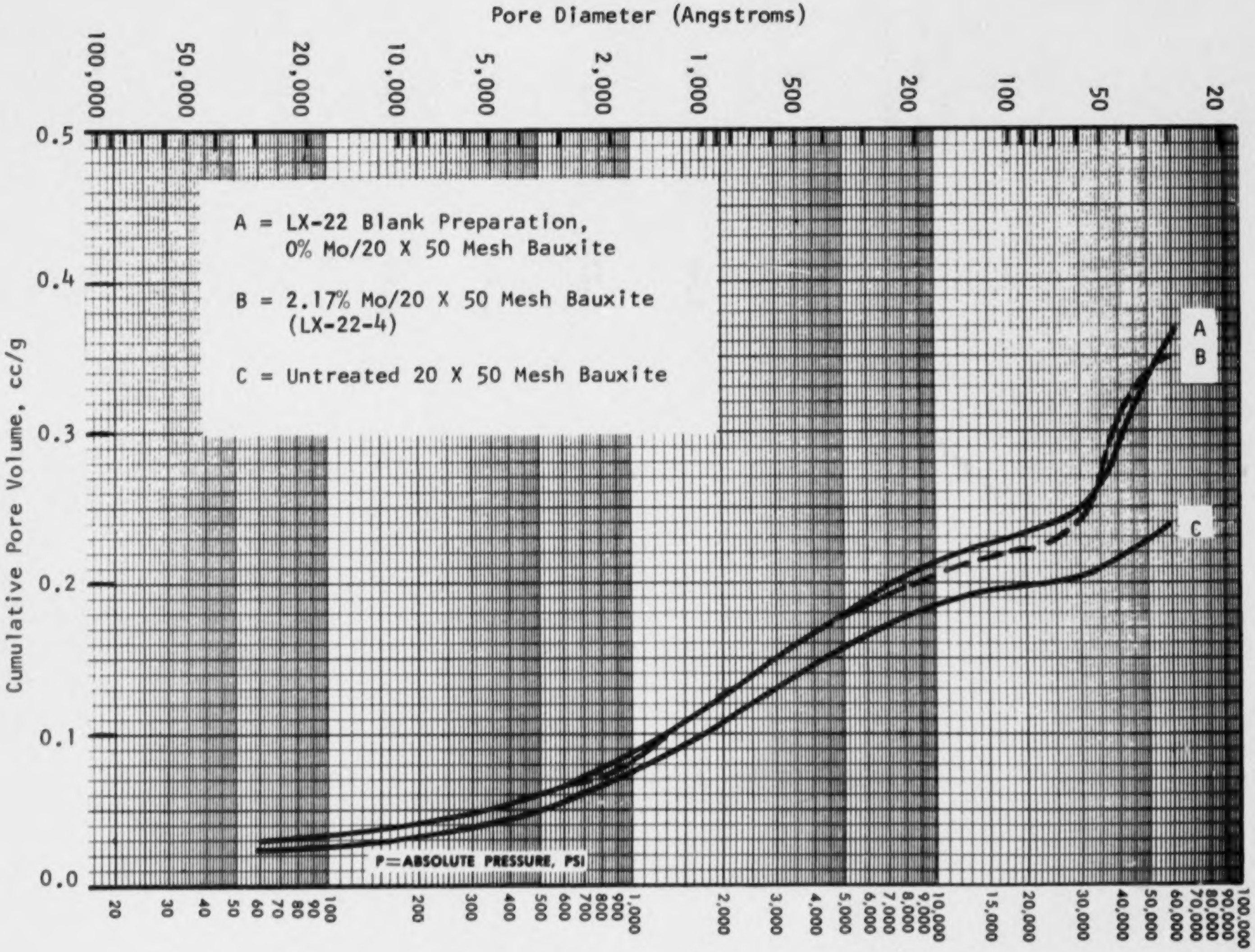


Figure 5. CUMULATIVE PORE SIZE DISTRIBUTION OF VARIOUS LX-22 PREPARATIONS

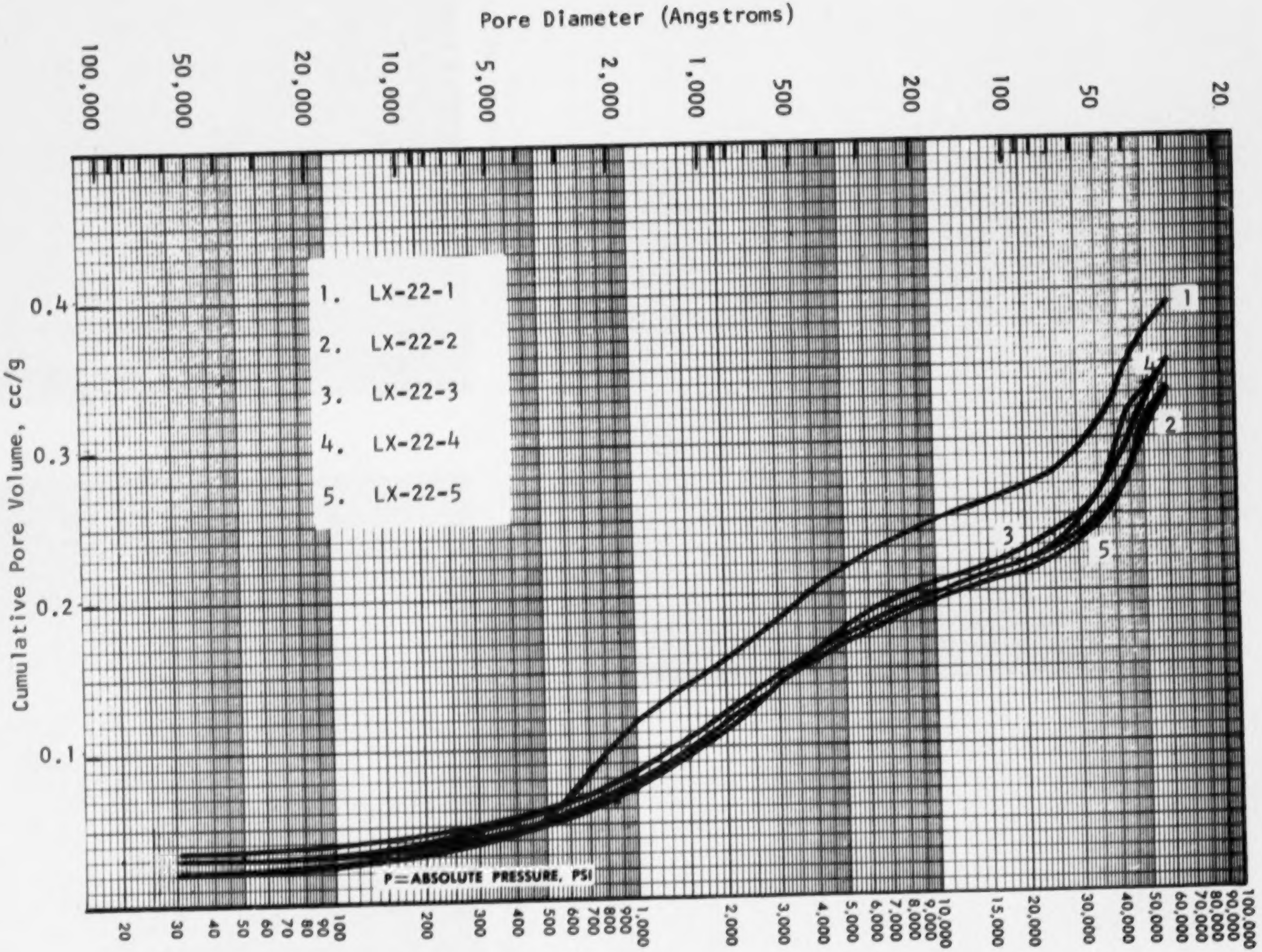
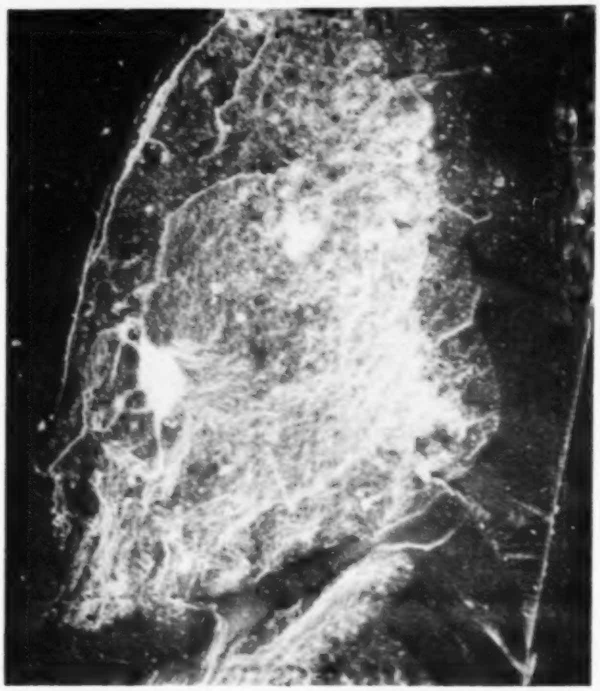
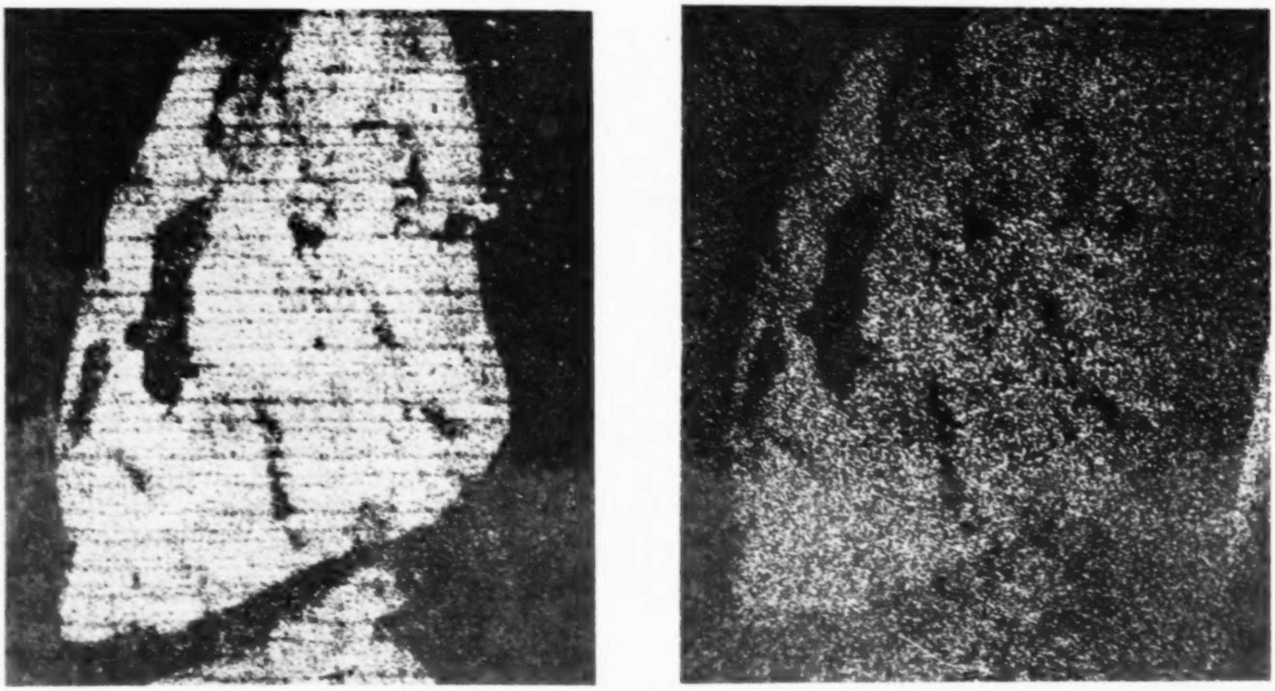


Figure 6. ELECTRON PROBE AND X-RAY STUDIES OF LX-22-1 AT 100X

LX-22-1 Electron Probe Scan





X-Ray Indication of
LX-22-1 Aluminum Distribution

X-Ray Indication of
LX-22-1 Molybdenum Distribution

thereby exposing their interior cross-section. By use of this technique, smearing of the molybdenum across the particle was avoided. Smearing could result if a grinding operation was employed to expose the interior of the small particles embedded in the epoxy matrix.

After preparation, the samples were introduced into a JEOLCO JCM-U3 scanning electron microscope with the capability of performing an X-Ray mapping of the cross-section of the pellet for both aluminum (the matrix metal) and molybdenum. The electron probe scan defines the shape of the particle being studied, as well as cracks (which are indicated by long thin lines), other surface irregularities, and inclusions of nonhomogeneous materials. These inclusions show up on the photograph as large, lighter colored areas. Light areas on the X-Ray scans indicate the presence of the element being scanned for while the dark areas indicate the absence of that element.

It is obvious from these pictures that the molybdenum is uniformly deposited over the cross-section of the catalyst. Analogous pictures are presented in Figure 7 for preparation LX-22-5.

PREPARATION OF DEMETALLIZED VACUUM RESIDUUM FEEDSTOCKS

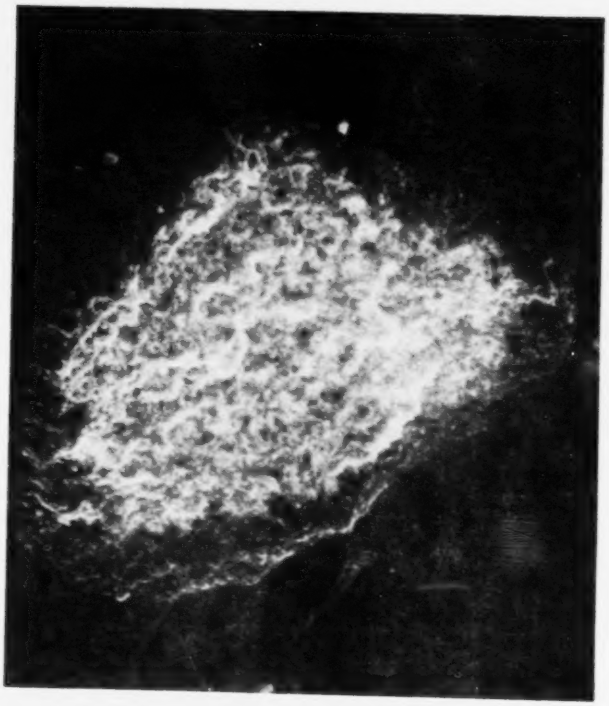
Three vacuum residuum feeds, Tia Juana vacuum residuum, Gach Saran vacuum residuum, and Bachaquero vacuum residuum, were used for our demetallization demonstration runs. Sufficient quantities of each feed were prepared to allow for lengthy desulfurization tests.

Both Tia Juana and Bachaquero crudes originate in the Lake Maracaibo area of Venezuela, while the Gach Saran crude is obtained from Iran. All three crudes represent major fields. In 1971, the total production of Bachaquero and Tia Juana crudes was 270,000,000 and 136,000,000 barrels, respectively. The estimated reserves of each are approximately ten times that. In 1971, the production rate of Gach Saran was 322,000,000 barrels with the reserves estimated at approximately twenty-five times that. These feeds are representative of major high metals crudes available in the world and are, for the most part, sold as export material. The daily production rates for these feeds are given in Table 9.

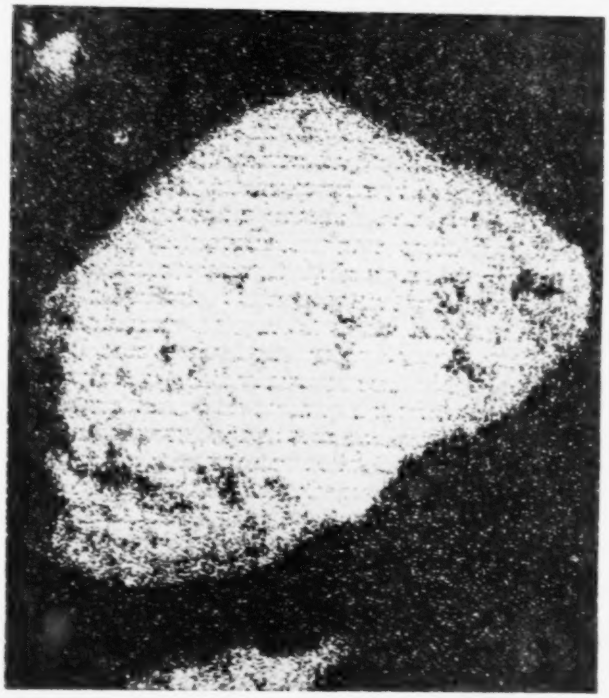
Interestingly, and perhaps because of their high metals content, the 1972 production of these crudes fell to 213, 111, and 316

Figure 7. ELECTRON PROBE AND X-RAY STUDIES OF LX-22-5 AT 200X

LX-22-5 Electron Probe Scan



X-Ray Indication of
LX-22-5 Aluminum Distribution



X-Ray Indication of
LX-22-5 Molybdenum Distribution

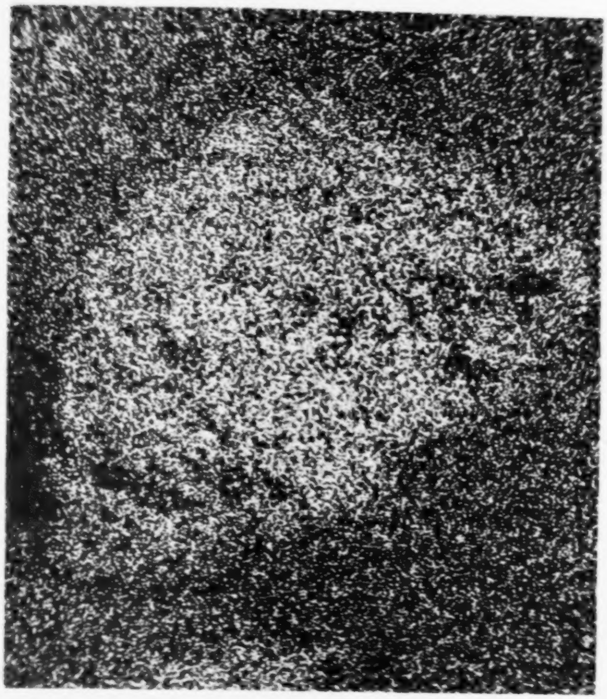


Table 9. 1971 VACUUM BOTTOMS PRODUCTION RATES FOR FEEDS STUDIED IN PROGRAM

Feed	1971 Crude Production B/D	Volume Percent Vacuum Bottoms on Crude	B/D Vacuum Bottoms
Gach Saran	882,000	21	185,000
Tia Juana	373,000	(30)	112,000
Bachaquero	740,000	32	237,000
	1,995,000		

million barrels for Bachaquero, Tia Juana, and Gach Saran, respectively.

The Bachaquero vacuum residuum for this purpose was obtained by distillation at the HRI® Laboratory of atmospheric residuum, which had been distilled from Bachaquero crude. The Tia Juana vacuum residuum was obtained from the Creole Petroleum Corporation, a subsidiary of Exxon.

Detailed inspections of the three vacuum residua are presented in Table 10. Summaries of operating data for these runs are given in Appendix D.

Long Term Demetallization Runs with Tia Juana Vacuum Bottoms

A total of four runs were made with Tia Juana vacuum bottoms to investigate the aging characteristics of the LX-22 catalyst and to produce feed for the desulfurization study. The first of these runs, Run 184-166, was part of the screening program and was made with preparation LX-22-1. In order to reduce the unit time required to achieve the age required, the spent catalyst from Run 184-166, which was a screening run, was recharged to a reactor and a new run, Run 185-210, was begun.

After following the original deactivation trend established in Run 184-166 for the eighth through eleventh days of operation, vanadium removal suddenly dropped from 70 to 60 percent and remained more or less constant at this level. A rapid drop off in the rate of both sulfur and nickel removal also occurred at this point.

Since this sudden drop off in catalyst activity could not be explained, another run, Run 185-211, using a new preparation, LX-22-3, of the two percent Mo/20 x 50 mesh activated bauxite, was used for this run. Figure 8 shows that, although the initial activity of the new preparation was the same as the original catalyst preparation (LX-22-1), the decline in vanadium removal was more rapid during the first seven days of operation. Unlike the first run, the demetallization activity decreased during the remainder of the run (days eight to fifteen) in a manner predicted by the results obtained during the first seven days of operation. However, after a total of fifteen days, the activity of the LX-22-3 was lower than that of LX-22-1.

Table 10. VACUUM RESIDUUM FEED INSPECTIONS

Feed	Tia Juana Vacuum Bottoms	Bachaquero Vacuum Bottoms	Gach Saran Vacuum Bottoms
Volume Percent on Crude	----	31.8	20.8
HRI Identification No.	2414	L-354	L-352
Gravity, °API	7.5	6.3	6.1
Sulfur, W %	2.91	3.44/3.63	3.30
Carbon, W %	85.37	83.94	82.93
Hydrogen, W %	10.68	10.29	10.40
Nitrogen, ppm	5400	5715	6037
RCR, W %	20.3	20.8	18.5
Vandium, ppm	550	685	324
Nickel, ppm	74	108	149
Viscosity, SFS @ 300°F	220	253	150
IBP-975°F			
Volume %	11.0	15	12.0
Gravity, °API		17.5	18.3
Sulfur, W %		2.28	2.00
975°F+			
Volume %	89.0	85.0	88.0
Gravity, °API		4.1	5.1
Sulfur, W %		3.51	3.40
RCR, W %		24.9	21.6

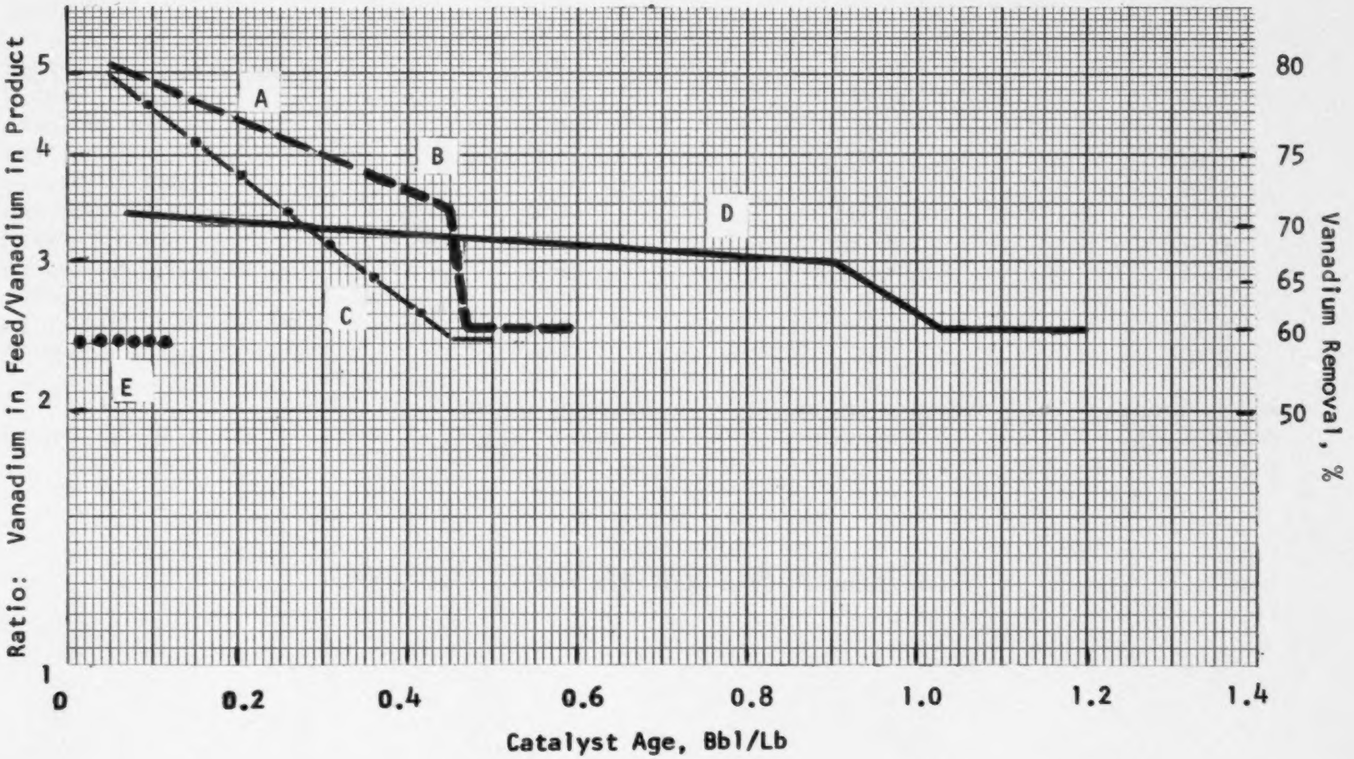
Figure 8. DEMETALLIZATION OF TIA JUANA VACUUM RESIDUUM

OVER 2% MOLYBDENUM/20 X 50 MESH BAUXITE

Feed Composition: 7.2-7.6°API, 2.9% Sulfur, 550 ppm Vanadium, 74 ppm Nickel

Operating Conditions

Run	Catalyst	Temperature °F	Pressure psig	$V_o/hr/V_r$
184-166	A. LX-22-1	790	2000	0.50
185-210	B. LX-22-1 (Recharged)	790	2000	0.50
185-211	C. LX-22-3	790	2000	0.50
184-174	D. LX-22-5	790	2000	0.75
184-167	E. 20 x 50 Mesh Activated Bauxite	790	2000	0.50



It was thought at first that the accelerated deactivation of LX-22-3 was due to a variation in catalyst properties or a variation in feed properties. Coincidentally, a new drum of feed was started approximately the same time that the sudden drop off in activity occurred during Run 185-210. This same drum was used throughout Run 185-211. The standard analyses indicated that this feed was essentially equivalent to that previously used and subsequent investigation revealed no significant difference among any of five different LX-22 catalyst preparations. The catalyst deactivation curves for these three runs (184-166, 185-210, and 185-211) and a fourth run (184-174), using yet another preparation of the two percent Mo/20 x 50 mesh bauxite catalyst, are also given in Figure 8. The last run was made at a space velocity of 0.75 $V_o/hr/V_r$ instead of the 0.50 $V_o/hr/V_r$ used in previous runs.

Although operation at 0.75 $V_o/hr/V_r$ results in a lower initial rate of vanadium removal, the rate of catalyst deactivation up to an age of 0.9 barrels per pound is so much lower that the useful life of the catalyst is double that obtained in the 0.5 $V_o/hr/V_r$ operations. Therefore, operation at lower severity (higher space velocity) results in a significant improvement in catalyst performance when considered on the basis of total vanadium removed per pound of catalyst. It is postulated that operation at the higher severity (lower space velocity) with this heavy vacuum residuum results in an accelerated rate of coke laydown which rapidly poisons the catalyst.

The catalyst analyses results presented in Table 11 clearly show the low level of carbon obtained in this last run, 8.54 percent, compared to the earlier runs that deactivated rapidly, 13.2 and 15.1 percent. Carbon on catalyst results from cracking reactions that are occurring simultaneously with demetallization and desulfurization. At the higher throughput, 0.75 $V_o/hr/V_r$, instead of 0.50 $V_o/hr/V_r$, the cracking reactions are minimized.

A run, Run 185-192, was made with unpromoted bauxite to generate comparable deactivation and demetallization data. This information is given in Figure 9. The deactivation of the activated bauxite seems to be controlled to a large extent by pore blockage. Figure 10 compares the difference in pore strucutre between virgin activated bauxite and spent material from Run 185-192, conducted with Tia Juana vacuum residuum. There is almost no change in the pore volume in pores larger than 2000 Å, while a substantial reduction is noted in pores between 2000 Å and 50 Å. All of the pore volume in pores less than 50 Å appears to be gone.

Table 11. ANALYSES OF SPENT DEMETALLIZATION CATALYST

Run No.	Feed	Weight Percent Element on Spent Catalyst			
		C	S	V	Ni
184-173	Gach Saran	7.1	11.33	11.02	2.85
184-174	Tia Juana	8.54	8.14	9.19	0.77
185-210	Tia Juana	13.2	6.18	5.32	5.48
185-211	Tia Juana	15.1	8.26	4.90	0.44
185-213	Bachaquero	14.81	7.18	8.74	0.87
185-215	Bachaquero	12.94	6.44	7.11	0.72
185-216	Bachaquero	9.68	6.69	6.42	0.68

Figure 9. DEMETALLIZATION OF TIA JUANA VACUUM RESIDUUM OVER 12 X 20 MESH ACTIVATED BAUXITE (HRI 2765)

Feed Composition	Operating Conditions
7.2°API	790°F
2.9% Sulfur	2000 psig
550 ppm Vanadium	4800 SCF H_2/Bbl
74 ppm Nickel	0.5-0.8 V_o/hr/V_r

Note: Data corrected to 0.5 V_o/hr/V_r on curve

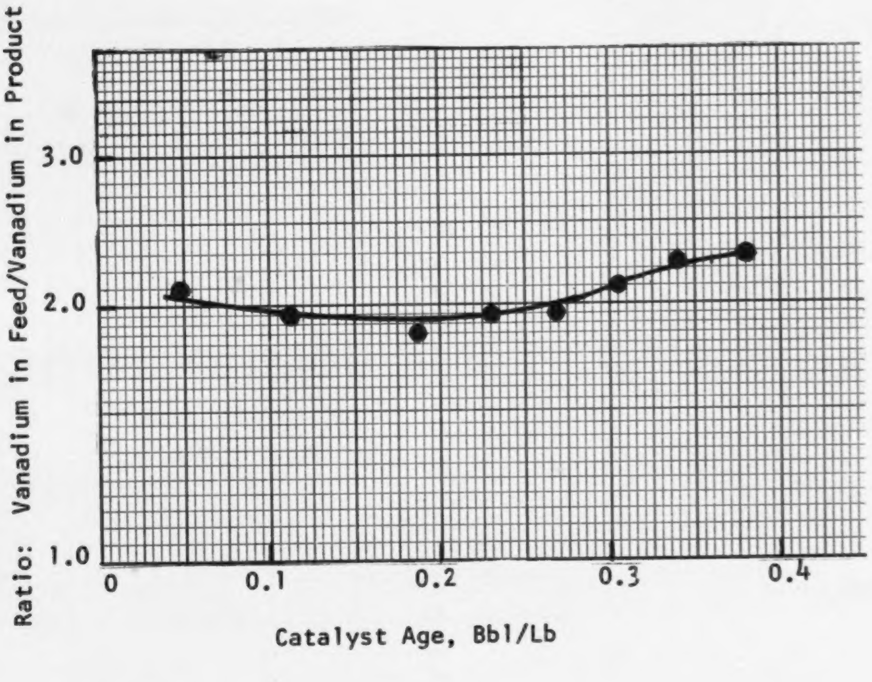
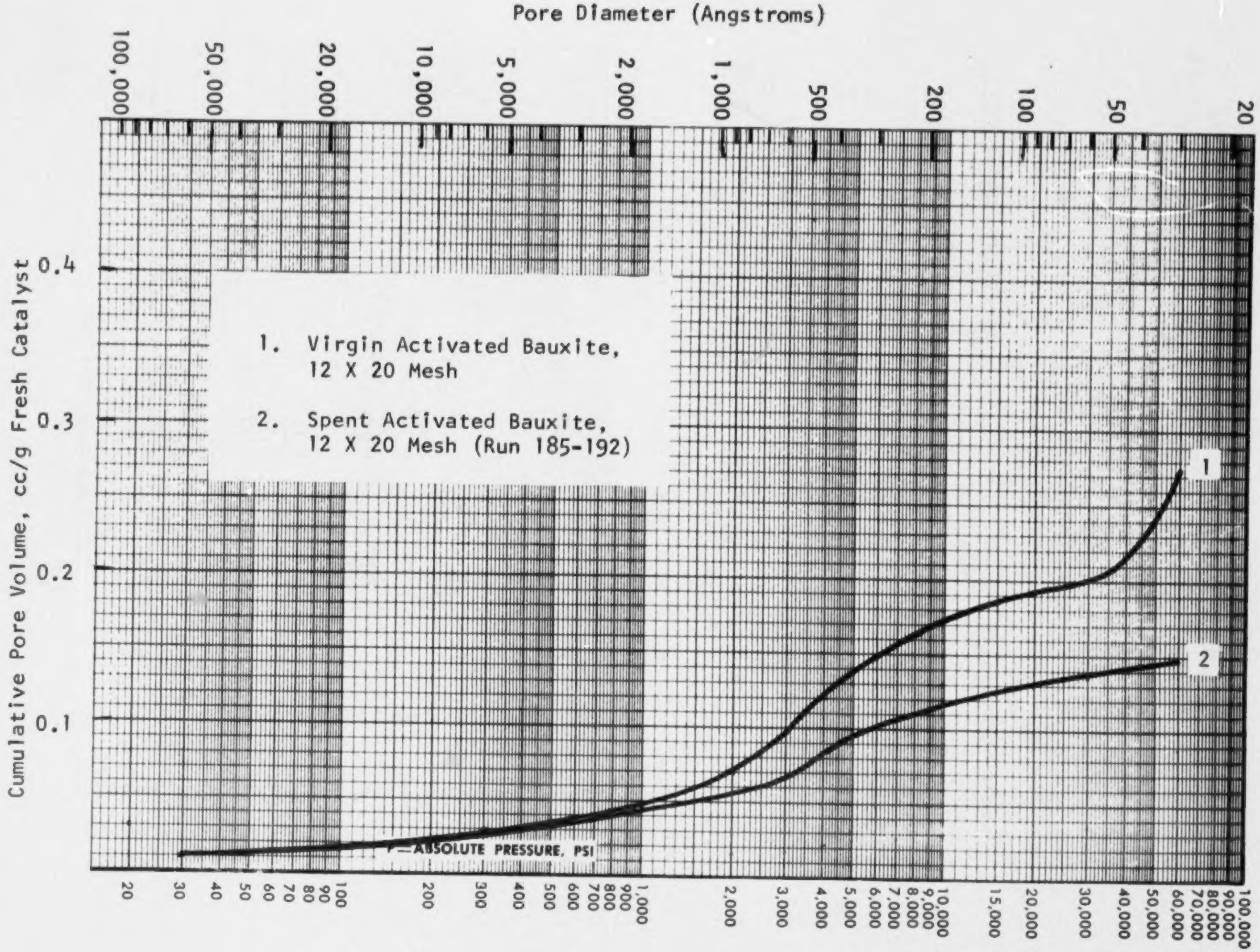


Figure 10. CHANGE IN ACTIVATED BAUXITE PORE SIZE DISTRIBUTION WHEN DEMETALLIZING TIA JUANA VACUUM RESIDUUM



Similar patterns of pore volume reduction are noted in Figures 11 and 12. The spent catalyst from Run 185-210 is compared with the LX-22-1 preparation that was used for that run in Figure 11. Figure 12 compares preparation LX-22-5 with the 184-174 dump catalyst. There are some differences in the pore volume of the LX-22-2 and LX-22-5 preparations and, therefore, the pore volume of the spent catalysts is also different. However, the difference between the fresh and spent catalyst pore volumes appears to be about the same in both cases. In spite of the difference in carbon level, 8.5 weight percent versus 13.2 weight percent, the amount of measurable pore volume seems about the same.

Long Term Demetallization Run with Bachaquero Vacuum Residuum

A total of four runs were made with the Bachaquero vacuum residuum to provide feed for desulfurization runs and aging data. Unpromoted bauxite was used to gather comparison data in a fifth run, Run 185-217.

The rapid deactivation of the catalyst as a result of low space velocity operation was further substantiated during the demetallization (Run 185-213) of Bachaquero vacuum residuum as shown in Figure 13. After operation at 0.75 $V_o/hr/V_r$ up to an age of 0.6 barrels per pound, the feed rate was reduced to 0.5 $V_o/hr/V_r$ and a rapid rate of deactivation followed. The Bachaquero demetallization was repeated at 0.75 $V_o/hr/V_r$ and demonstrated that rapid deactivation could be avoided by operation at a sufficiently high feed rate. It is believed that operations at the lower space velocity resulted in the rapid deposition of coke on the catalyst resulting in deactivation. Since a similar rapid deactivation occurred during the demetallization of Tia Juana vacuum residuum at 0.50 $V_o/hr/V_r$, there appears to be a limit to the severity at which the demetallization of these two feeds can be carried out. This limits the extent to which these feeds can be demetallized prior to desulfurization. However, the metals-containing species remaining in these demetallized feeds deposit on a desulfurization catalyst at a substantially lower rate than those removed from the feed by the demetallization catalyst. Therefore, although these feeds cannot be demetallized to levels in excess of 75 percent vanadium removal, the rates of metals deposition on a high activity desulfurization catalyst during subsequent desulfurization operations are low enough to prevent rapid deactivation of this more expensive catalyst.

Figure 11. CHANGE IN PORE SIZE DISTRIBUTION

OF LX-22-1 WHEN DEMETALLIZING TIA JUANA VACUUM RESIDUUM

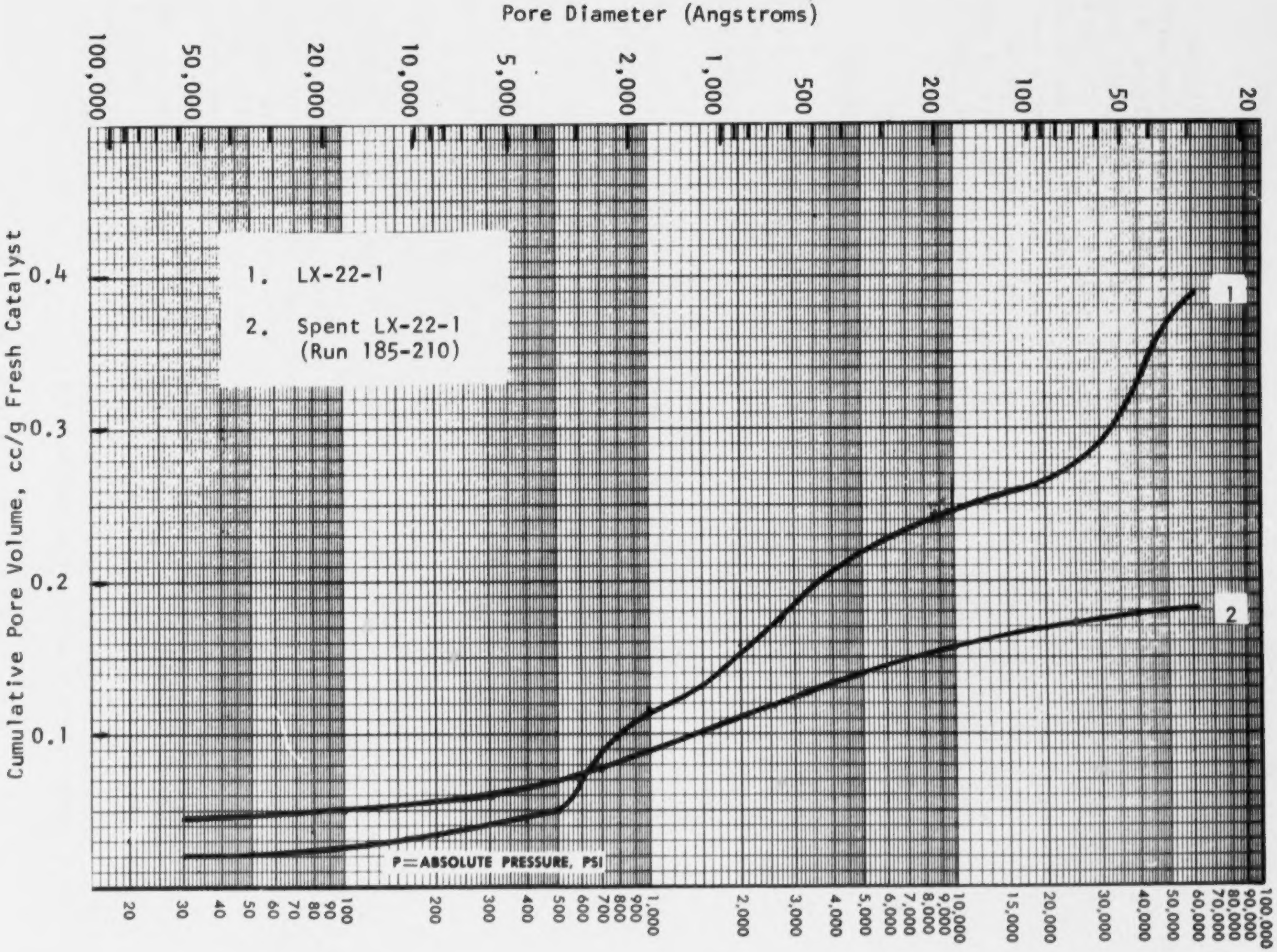


Figure 12. CHANGE IN PORE SIZE DISTRIBUTION OF LX-22-5 WHEN DEMETALLIZING TIA JUANA VACUUM RESIDUUM

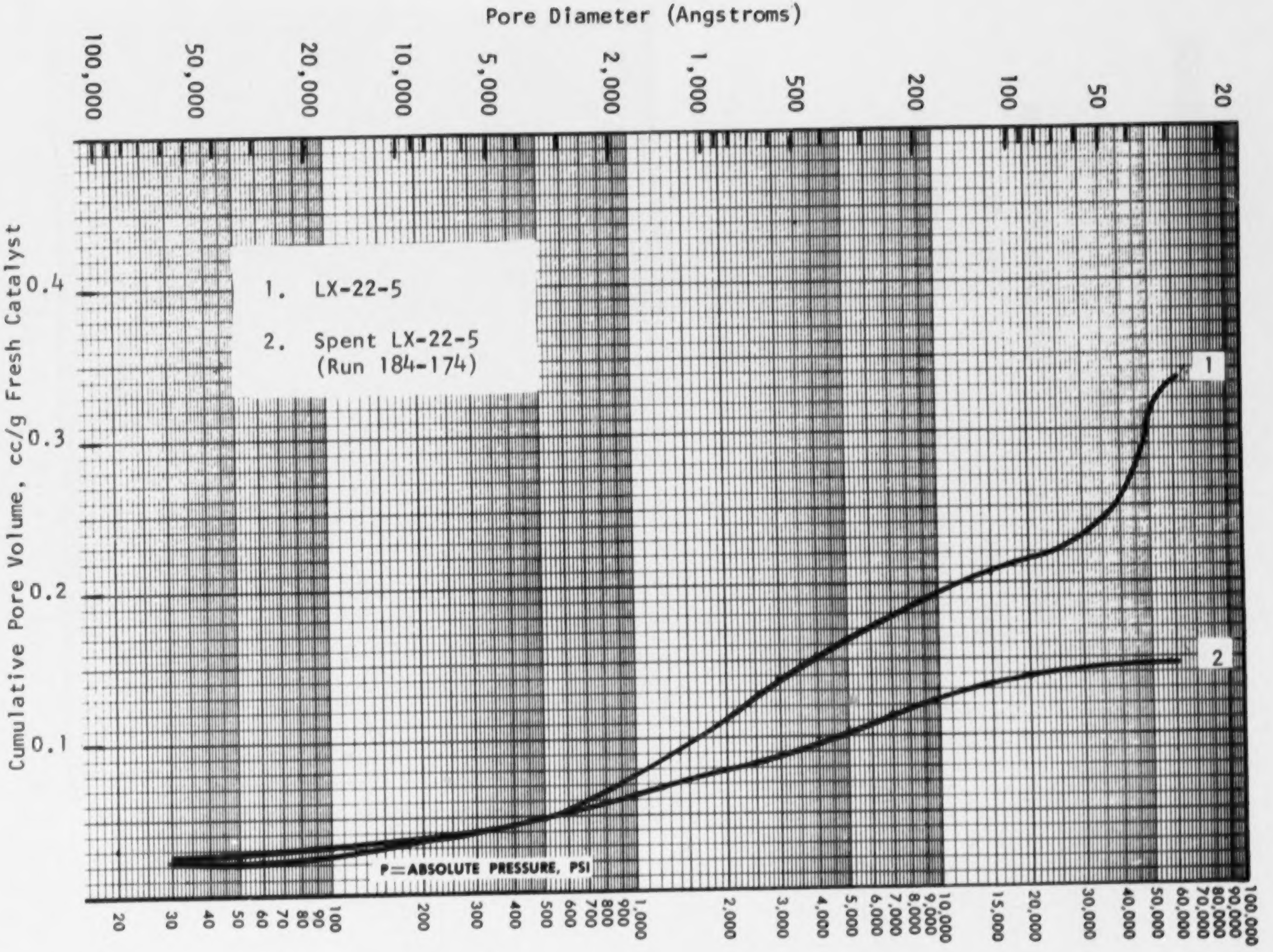
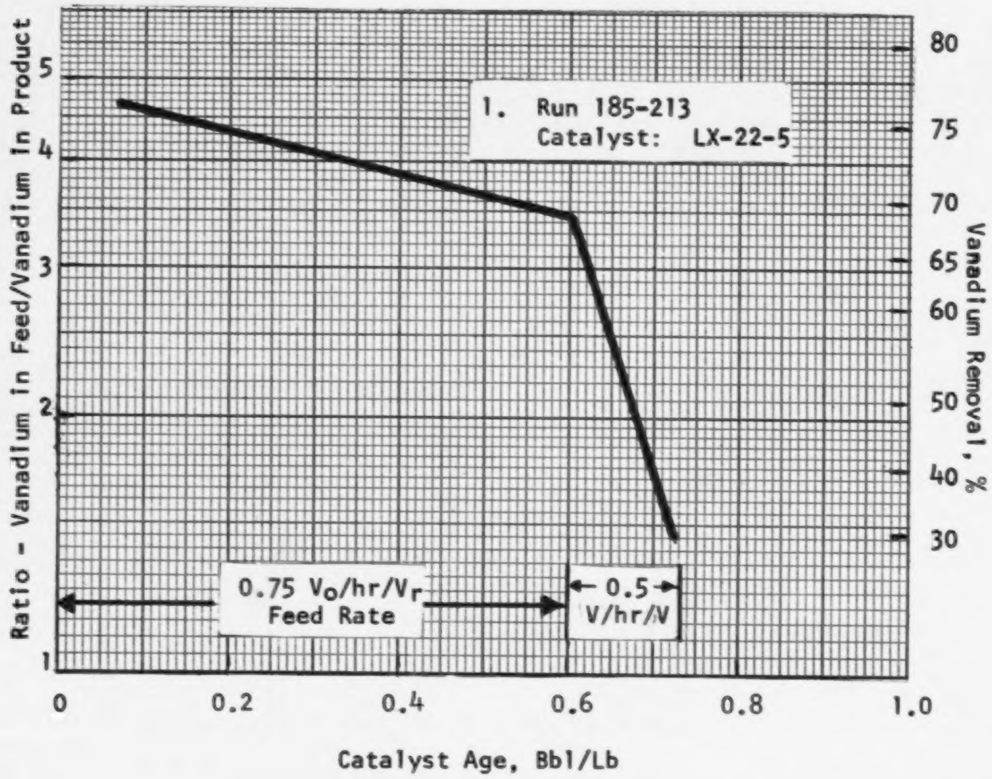


Figure 13. DEMETALLIZATION OF BACHAQUERO VACUUM RESIDUUM OVER 2% MOLYBDENUM/20 X 50 MESH BAUXITE

Feed Composition	Operating Conditions
6.3 °API	790 °F
3.4 % Sulfur	2000 psig
685 ppm Vanadium	4000 SCF H_2.Bbl
108 ppm Nickel	0.75 $V_o/hr/V_r$ (0.055 Bbl/D/Lb)

Note: Data at 0.5 $V_o/hr/V_r$ corrected to 0.75 $V_o/hr/V_r$ on curve



These five runs have been corrected to standard operating conditions and the deactivation curves are presented in Figure 14. Figures 15 and 16 show the reduction in pore volume which occurred in Runs 185-215 and 185-216. On a total loss of pore volume basis, it is similar to that obtained in the Tia Juana operation. As in the Tia Juana operation, the lower severity operation of Run 185-216 did not result in a lesser loss of pore volume than was experienced in the higher severity operation. It may be that the higher severity operation caused carbon deposition at the pore mouth which resulted in added diffusional resistance within the catalyst. This type of deposit would not materially affect total pore volume.

Demetallization of Gach Saran Vacuum Residuum

Demetallization of Gach Saran vacuum residuum was carried out in Run 184-173. The operating conditions and the results of that operation are summarized in Figure 17. The most noteworthy thing about this operation was the ease with which the demetallization was accomplished. Significantly higher levels of demetallization were obtained with this feed than with the Bachaquero or Tia Juana vacuum bottoms. The activity decline was also modest when compared with the results of the other feeds. The spent catalyst results from these operations were presented previously in Table 11. They show the highest level of vanadium loading, along with the lowest carbon level, 11.0 and 7.0 percent, respectively. The ease of vanadium removal makes it desirable to remove as much as possible since it has been determined that the ease of removal in the demetallization stage correlates well with the ease of removal in the desulfurization stage. Therefore, in order to protect the desulfurization catalyst, it is necessary to go to higher levels of demetallization in the demetallization stage, but, of course, it is not as difficult to achieve for this feed.

The type of reduction in pore volume previously noted for Tia Juana vacuum residuum was obtained with Gach Saran vacuum residuum. This is shown in Figure 18.

Figure 14. DEMETALLIZATION OF BACHAQUERO VACUUM RESIDUUM OVER 2% MOLYBDENUM/20 X 50 MESH BAUXITE

Feed Composition: 6.1-6.3°API, 3.44-3.63% Sulfur,
685 ppm Vanadium, 108 ppm Nickel

Run	Catalyst	Temperature °F	Pressure psig	$V_o/hr/V_r$
185-213	A. LX-22-5	790	2000	0.5-1.0
185-214	B. LX-22-4	790	2000	0.7-1.0
185-215	C. LX-22-4	790	2000	0.7-1.0
185-216	D. LX-22-3	790	2000	0.7-1.0
185-217	E. Unpromoted Bauxite	790	2000	0.6

Note: All Data Corrected to 0.75 $V_o/hr/V_r$ on Curve

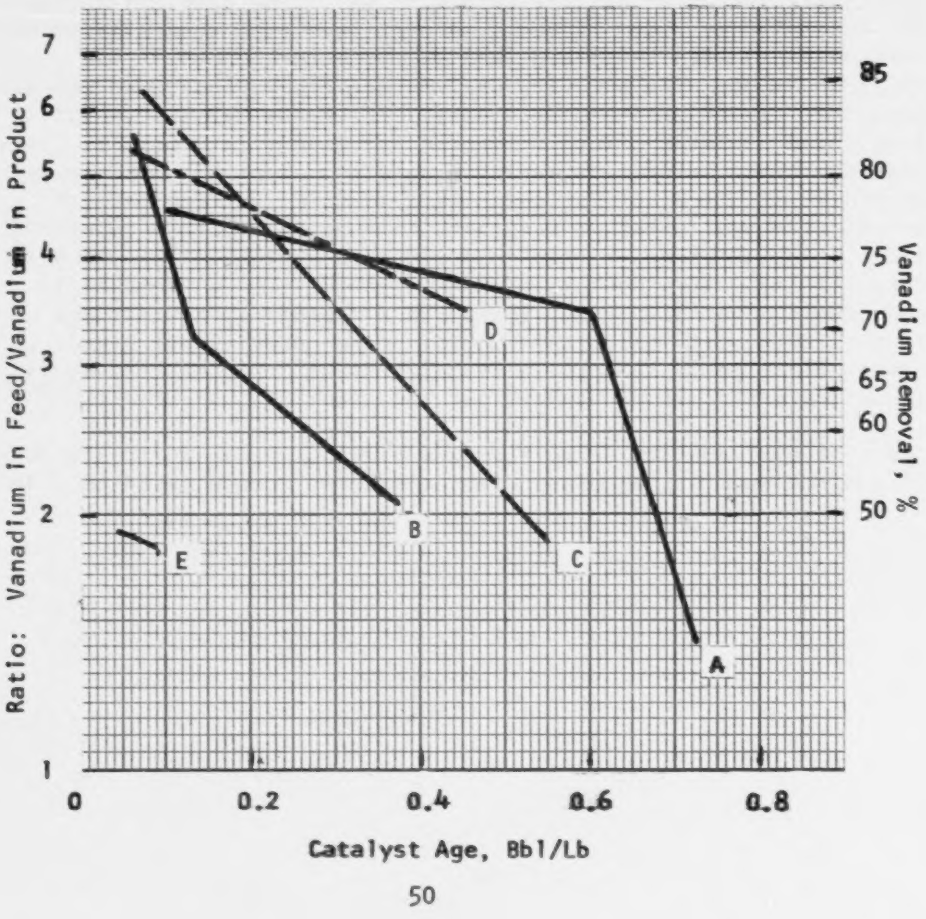


Figure 15. CHANGE IN PORE SIZE DISTRIBUTION OF LX-22-4 WHEN DEMETALLIZING BACHAQUERO VACUUM RESIDUUM

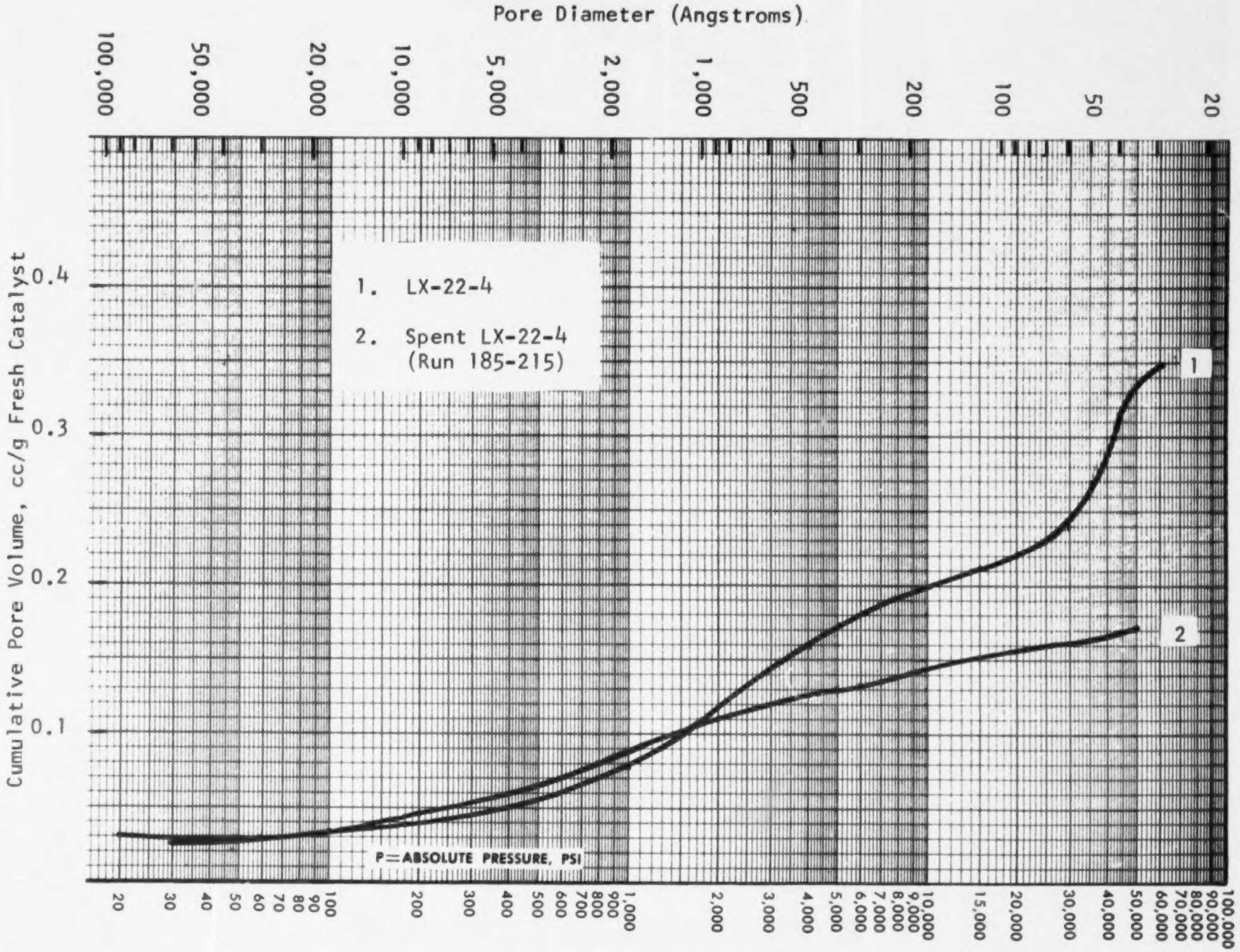


Figure 16. CHANGE IN PORE SIZE DISTRIBUTION OF LX-22-3 WHEN DEMETALLIZING BACHAQUERO VACUUM RESIDUUM

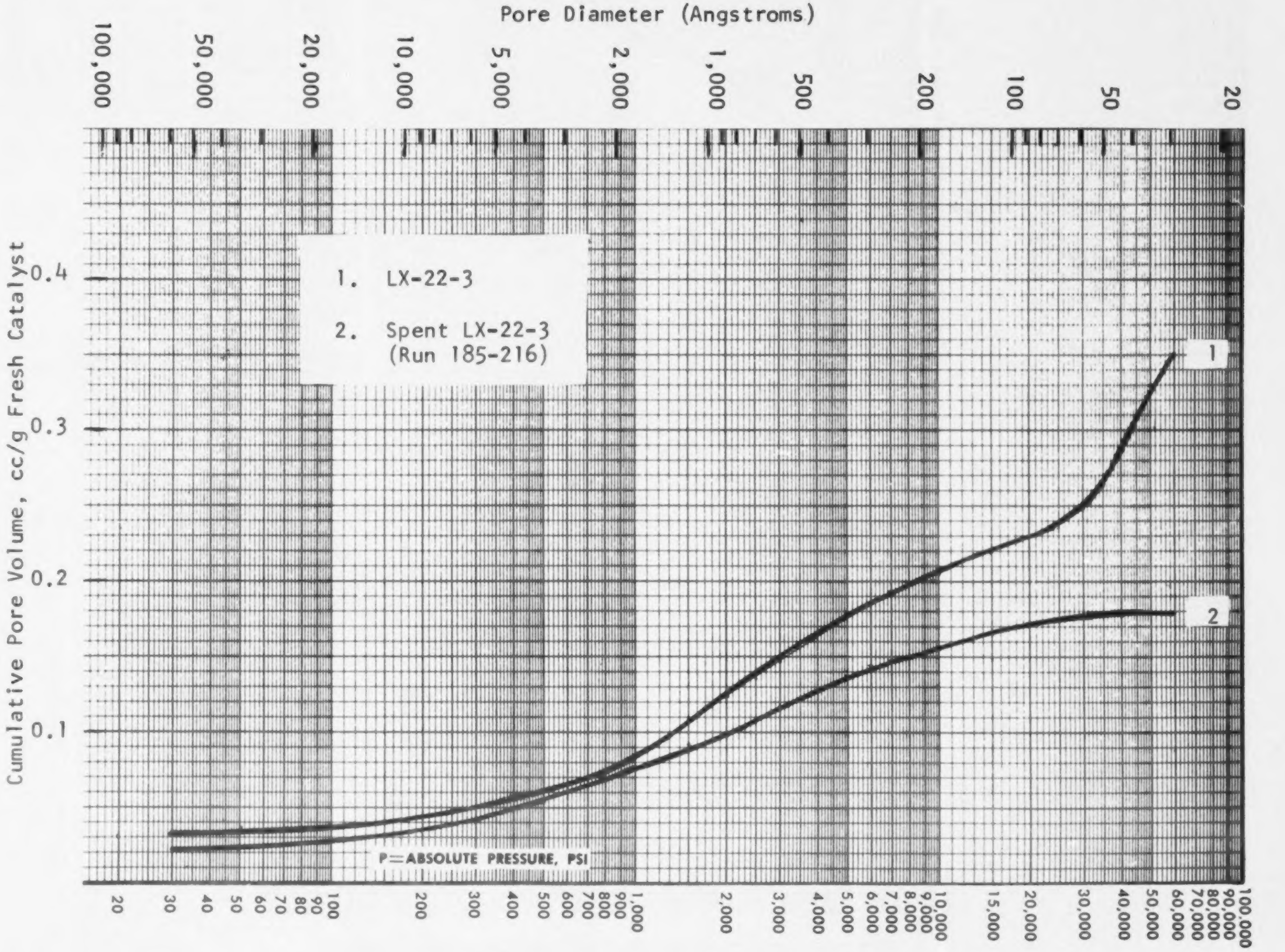


Figure 17. DEMETALLIZATION OF GACH SARAN VACUUM RESIDUUM

OVER 2% MOLYBDENUM/20 X 50 MESH BAUXITE

Run 184-173 - Catalyst LX-22-2

Feed Composition

6.1 °API
3.3% Sulfur
328 ppm Vanadium
147 ppm Nickel

Operating Conditions

790°F
2000 psig
4000 SCF H_2/Bbl
0.75 $V_o/hr/V_r$ (0.055 B/D/Lb)

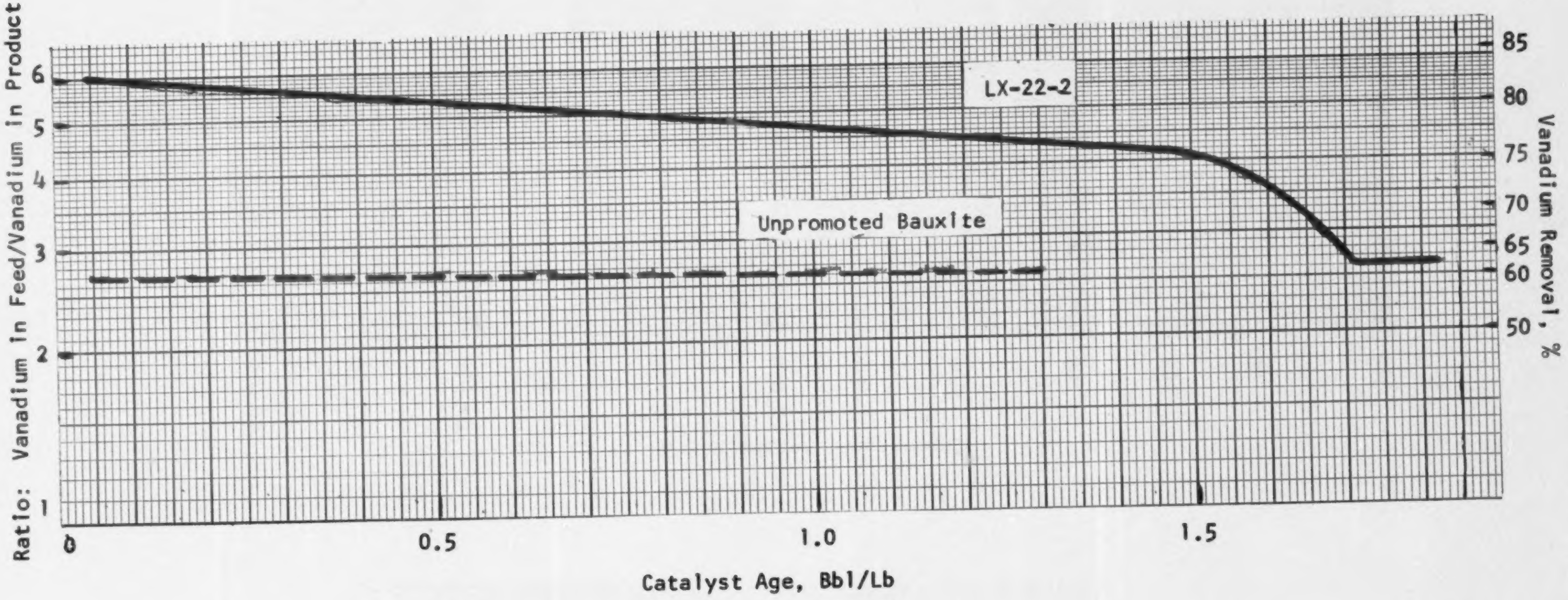
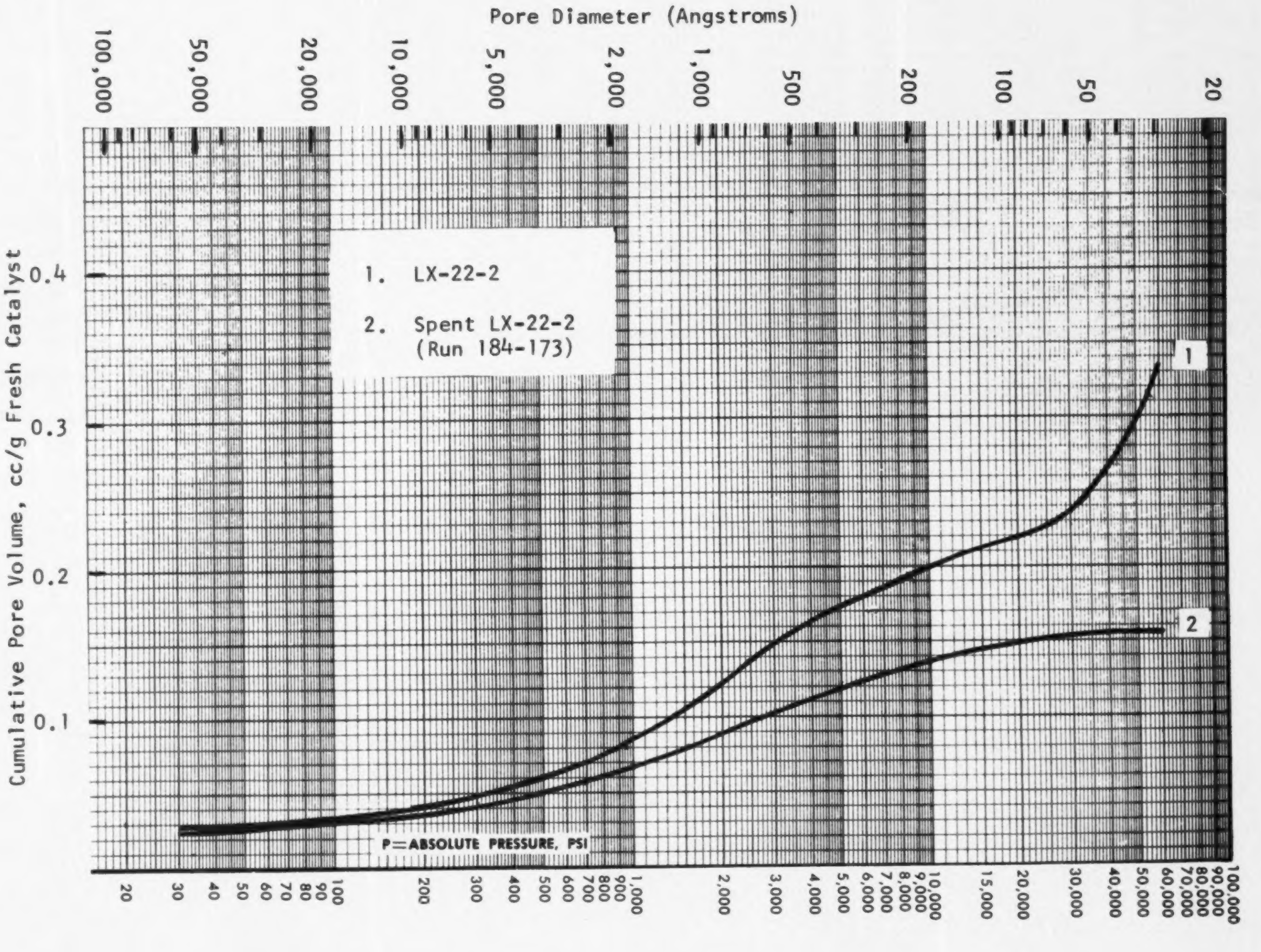


Figure 18. CHANGE IN PORE SIZE DISTRIBUTION OF LX-22-2 WHEN DEMETALLIZING GACH SARAN VACUUM RESIDUUM



FEEDSTOCK PREPARATION

Demetallized residua from various test runs were collected and blended so that a feed having constant properties could be fed to the desulfurization step. The products that were blended to make the feed to the desulfurization unit are listed in Table 12. The requirement for blending was made necessary in the case of the Bachaquero and Tia Juana vacuum bottoms residua since some difficulties were encountered in maintaining the desired demetallization level when higher severity operations were attempted. However, since the primary criteria for selection for the desulfurization unit was the metals content of the feed, it was felt that the use of material blended from various operations, as long as the metals content was about the same for all components blended, would result in a justifiable desulfurization operation. The inspections on the blended feeds for each of the desulfurization runs are listed in Table 13.

CATALYST SELECTION

The catalyst selected for the desulfurization operations was a high activity American Cyanamid preparation. The catalyst had shown the ability to produce low sulfur products from vacuum residua in other test work not covered by this program. Its small particle size, ~0.02-inch diameter, makes it particularly resistant to deactivation due to metals deposition. It was on this basis then, that this catalyst was selected as the most likely to be part of a large-scale demetallization-desulfurization combination process. The properties of the catalyst are summarized in Table 14.

OPERATING CONDITIONS

Desulfurization operating conditions were selected so that a maximum degree of desulfurization with a minimum hydrogen utilization would be obtained. All runs were conducted in the same fixed bed downflow apparatus previously described. Each run was conducted at 760°F, 2000 psig hydrogen partial pressure, ~4500 SCF of hydrogen per barrel, and a space velocity of 0.106 barrels of oil per day per pound of catalyst. The runs were generally carried out to

Table 12. COMPOSITION OF DEMETALLIZED RESIDUA

FED TO THE DESULFURIZATION REACTOR

Feed	Demetallized Tia Juana Vacuum Residuum	Demetallized Bachaquero Vacuum Residuum		Demetallized Gach Saran Vacuum Residuum
HRI Number	L-357	L-358	L-359	L-356
Products Blended to make Composite Feed	185-205	185-213	185-215 (Periods 3-5)	184-173 (Periods 5-22)
	185-210	185-214	185-216 (Periods 1-8)	
	185-211			
	184-166			
	184-169			
	184-174			

Table 13. DEMETALLIZED FEED INSPECTIONS

Feed	Demetallized Tia Juana Vacuum Bottoms	Demetallized Bachaquero Vacuum Bottoms		Demetallized Gach Saran Vacuum Bottoms
Catalyst	LX-22	LX-22	LX-22	LX-22
HRI Identification No.	L-357	L-358	L-359	L-356
Gravity, °API	13.0	13.5	12.0	12.1
Sulfur, W %	1.50	1.67	1.61	1.31
Carbon, W %	86.65	85.86		85.79
Hydrogen, W %	10.79	10.87		11.25
Nitrogen, ppm	4984	5686		
RCR, W %	13.7	14.7		14.0
Vanadium, ppm	177	180	182	67
Nickel, ppm	47	71	60	58
IBP-975°F				
Volume %	20.0	23.3		23.3
Gravity, °API	19.8	19.1		19.2
Sulfur, W %	0.92	1.02		0.81
975°F+				
Volume %	70.7	63.4		66.7
Gravity, °API	9.6	7.1		7.7
Sulfur, W %	1.75	1.96		1.75
RCR, W %	19.6	22.3		19.9
Vanadium, ppm	222			

Table 14. SUMMARY OF INSPECTIONS ON AMERICAN CYANAMID 0.02" HIGH ACTIVITY BEADED CATALYST

HRI Identification Number	3104
Physical Properties	
Surface Area, M^2/g	250
H_2O Pore Volume, cc/g	0.67
Hg Pore Volume, cc/g	0.62
Screen Analysis, U.S. Sieve No.	
+20	1.3
20/30	16.9
30/40	76.2
40/50	5.0
50/70	0.5
70/100	0.1
-100	----
Chemical Analysis, W %	
MoO_3	(15.0)
CoO	(3.0)

a catalyst age between 2.6 and 3.1 barrels per pound. Runs of this duration provide an accurate measure of the catalyst deactivation rate and provide information about ultimate catalyst utilization required to get a given product desulfurization level. In addition, additional information was gathered on the amount of metals laydown on the catalyst for a given operation. Detailed operating conditions for each run of this series is presented in Appendix E.

RESULTS

The demetallized Gach Saran vacuum residuum was desulfurized in Run 201-69 until a catalyst age of 2.63 barrels per pound was achieved. Run 201-70, with a demetallized Bachaquero vacuum residuum, was run to a catalyst age of 2.72 and Run 184-175, with a demetallized Tia Juana vacuum residuum, was run to a catalyst age of 3.09 barrels per pounds. The operating conditions were such that correlations could be used to predict the operating conditions required for 0.5 percent sulfur product in an equilibrium catalyst situation. The experimental data is plotted in Figures 19, 20, and 21 for each of the feedstocks. The outstanding result noted from these operations is the very low rate of catalyst deactivation throughout the run. Of course, in a commercial operation, the ultimate catalyst lives would be on the order of 10.0 barrels per pound, but little was to be gained from further continuation of these runs in that the deactivation can be extrapolated with confidence.

CATALYST DEACTIVATION

The analyses of the spent catalyst from the desulfurization operation is presented in Table 15. The amount of vanadium contained on these catalysts is low, of course, in comparison to that which would have been observed if the feeds had not been demetallized. The data presented in Table 16 show that the absolute amount of vanadium removal over the length of the run was highest for the Bachaquero feed and followed by the Gach Saran and Tia Juana feeds, respectively. The amount of vanadium removed in the desulfurization operation for the three feeds were 35, 24, and 26 ppm, respectively. Comparable data for nickel are 26, 23, and 26 ppm, respectively.

Figure 19. DESULFURIZATION OF DEMETALLIZED GACH SARAN VACUUM RESIDUUM

Run 201-69

Feed Composition

12.1°API
1.31% Sulfur
67 ppm Vanadium
58 ppm Nickel

Operating Conditions

760°F
2000 psig
8300 SCF H_2/Bbl
1.0 V_o/hr/V_r
0.106 B/D/Lb

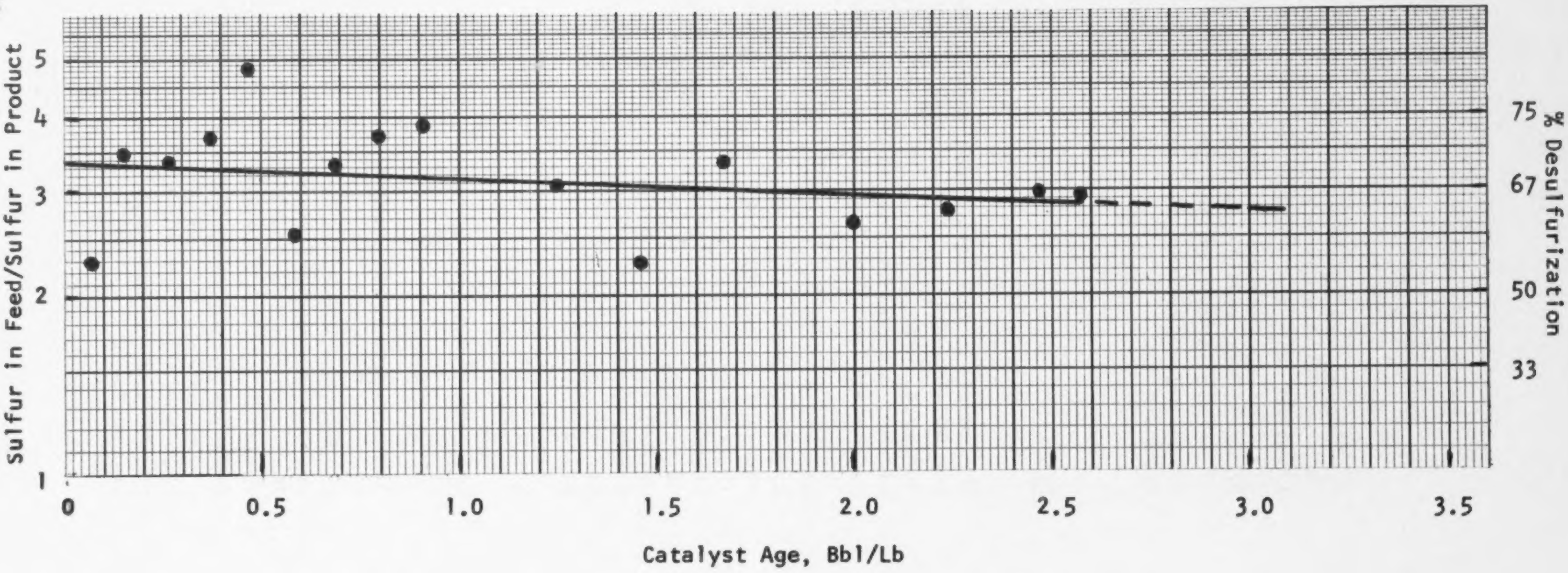


Figure 20. DESULFURIZATION OF DEMETALLIZED BACHAQUERO VACUUM RESIDUUM

Run 201-70

Feed Composition

12-13.5°API
1.64% Sulfur
181 ppm Vanadium
60-71 ppm Nickel

Operating Conditions

760°F
2000 psig
4800 SCF H_2/Bbl
1.0 V_o/hr/V_r
0.106 B/D/Lb

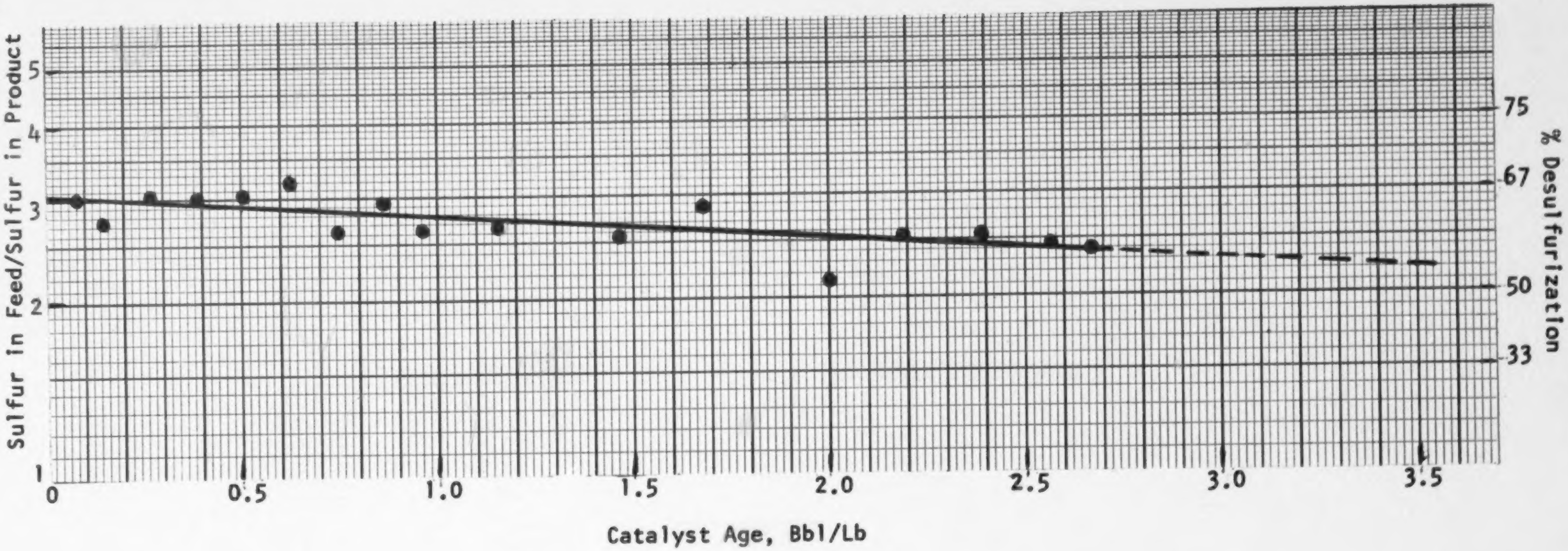


Figure 21. DESULFURIZATION OF DEMETALLIZED TIA JUANA VACUUM RESIDUUM

Run 184-175

Feed Composition	Operating Conditions
13.0°API	760°F
1.50% Sulfur	2000 psig
177 ppm Vanadium	4500 SCF H_2/Bbl
47 ppm Nickel	1.0 V_o/hr/V_r
	0.106 B/D/Lb

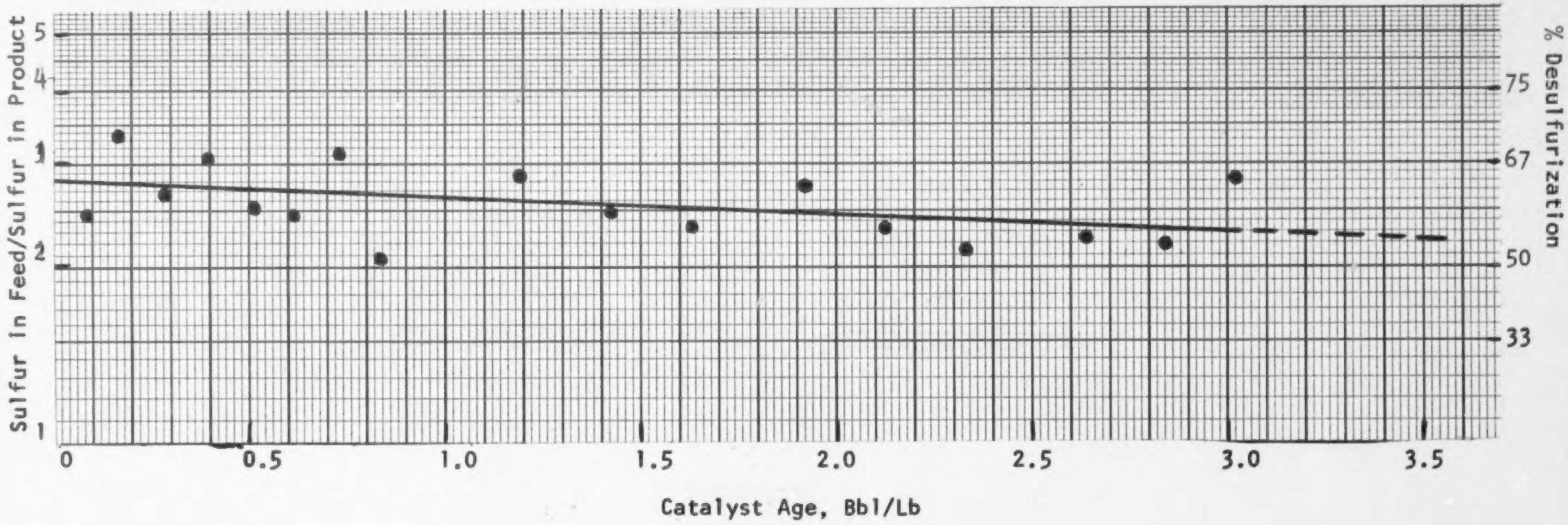


Table 15. ANALYSES OF SPENT DESULFURIZATION CATALYST

Run No.	Demetallized Vacuum Residuum Feed	Weight Percent Element on Spent Catalyst			
		C	S	V	Ni
201-69	Gach Saran	15.67	5.11	1.55	1.01
201-70	Bachaquero	13.71	5.36	2.72	0.86
184-175	Tia Juana	14.78	4.75	0.85	0.26

Table 16. VANADIUM AND NICKEL BALANCES FROM DESULFURIZATION RUNS

Run Number	201-69		201-70		184-175	
Desulfurization Catalyst Age, Bbl/Lb	2.63		2.72		3.09	
Feed	Demetallized Gach Saran Vacuum Resid		Demetallized Bachaquero Vacuum Resid		Demetallized Tia Juana Vacuum Resid	
V, ppm	67		180-182		177	
Ni, ppm	58		60-71		47	
	Grams	W % Feed	Grams	W % Feed	Grams	W % Feed
In						
Feed						
Vanadium	3.99		10.96		12.05	
Nickel	3.45		3.82		3.20	
Out						
Vanadium						
Liquid Product	2.76	69.2	8.96	81.8	10.27	85.3
On Catalyst	1.27	31.8	2.27	20.7	0.62	5.1
Total	4.03	101.0	11.23	102.5	10.89	90.4
Nickel						
Liquid Product	2.16	62.5	2.82	73.7	2.95	92.2
On Catalyst	0.84	24.3	0.69	18.0	0.20	6.3
Total	3.00	86.8	3.51	91.7	3.15	98.5

The amount of vanadium in the original feeds that deposited on the catalyst is presented in Table 17. For Gach Saran, Bachaquero, and Tia Juana, it amounts to 7.4, 5.1, and 1.6 percent, respectively. These data show the effectiveness of utilizing a demetallization step before desulfurization in order to protect the life of the catalyst. The advantage of using a demetallization catalyst having some desulfurization activity is best gained by a reduction in the severity of the desulfurization step. The severities utilized here for obtaining these low sulfur products are certainly within the realm of today's commercial heavy oil treating experience. It should also be noted that metals removal during desulfurization, such as encountered in these experiments, is similar to current commercial operations where atmospheric residua having low levels of vanadium, such as are obtained from Kuwait and Light Arabian crudes, are being desulfurized to low levels.

PRODUCT INSPECTIONS

Detailed product inspections were obtained on two products from each of the desulfurization runs, one product from near the beginning of the run, and the second one from near the end of the run. These inspections, which are in Appendix F, are provided so that enough information is available to those who might use this data in the future for considering the possibility of splitting the product into various fractions and marketing them according to their various sulfur levels. This combination may result in a higher total net value of the products.

An overall summary table of the demetallization and desulfurization process to produce 0.5 weight percent 400°F+ fuel oil from the three vacuum residua is presented in Table 18. In all cases, the yield of fuel oil product exceeds 96 volume percent on residuum charged. The balance of the liquid product, averaging about eight percent is C_4-350°F naphtha, which is quite valuable in today's economy.

Table 17. EFFECT OF METALS REMOVAL FROM HIGH METALS FEED ON METALS LAYDOWN ON CATALYST

Vacuum Residuum Feed	Run No.	Original Feed		Demetallized Feed		Metals Removed from Virgin Feed in Demetallization Step		% of Demetallized Feed Metals on Desulfurization Catalyst		Grams of Metals from Feed on Catalyst		Desulfurization Catalyst Quantity, Grams
		V	Ni	V	Ni	% V	% Ni	V	Ni	V	Ni	
Gach Saran	201-69	328	147	67	58	80	61	32	24	1.27	0.84	65.7
Bachaquero	201-70	685	108	181	65	74	40	21	18	2.27	0.69	64.4
Tia Juana	184-175	550	74	177	47	68	36	5	6	0.62	0.20	64.3

Table 18. SUMMARY OF RESULTS ON THE DEMETALLIZATION AND DESULFURIZATION OF VACUUM RESIDUA

(Feed and Product Analyses)

Vacuum Bottoms	Raw Feed	Demetallized Feed	Desulfurized Product[a]
Gach Saran			
% Sulfur	3.4	1.3	0.5
Vanadium, ppm	328	67 (80% V Removal)	43
Nickel, ppm	147	58	35
C_4-400°F+, V %	---	---	8.2
400°F+. V %	---	---	96.2
Tia Juana			
% Sulfur	2.9	1.5	0.5
Vanadium, ppm	550	177 (68% V Removal)	141
Nickel, ppm	74	47	41
C_4-400°F, V %	---	---	9.0
400°F+. V %	---	---	96.2
Bachaquero			
% Sulfur	3.6	1.7	0.5
Vanadium, ppm	685	180 (74% V Removal)	145
Nickel, ppm	108	71	45
C_4-400°F, V %	---	---	10.0
400°F+, V %	---	---	96.9

a. Sulfur and metals analyses are for 400°F+ fuel oil fractions. Product yields are based on volume of raw feed.

SUMMARY OF TRACE ELEMENTS

At the inception of this project, the Environmental Protection Agency requested that measurements be made on the trace elements that are normally present in the three vacuum residuum feeds and the demetallized and desulfurized products that were obtained. Neutron activation analysis was selected as the most promising analytical technique by which this goal could be accomplished.

A summary of the quantitative neutron activation analyses (N.A.A.) run by Gulf Radiation Technology on the raw Bachaquero, Gach Saran, and Tia Juana vacuum residua is presented in Table 19. Only the calculated upper limits, i.e., the maximum concentration at which the element may be present and avoid detection, were obtained for the remainder of the elements scanned, which are indicated in Table 20. Besides nickel and vanadium, which were run routinely in the Laboratory, only four elements (manganese, arsenic, copper, and silver) that are of the most interest to the Environmental Protection Agency, could be determined quantitatively. Without costly sample preparation techniques, N.A.A. has very limited capabilities for determining the extent of removal of the majority of trace elements of interest in the demetallization and desulfurization operations. For this reason, further trace elements analyses using the N.A.A. technique were suspended.

Three selected products of demetallized Tia Juana vacuum residuum were sent to Gulf Radiation Technology for N.A.A. No other product samples were sent out since it was discovered that the levels of most of the elements in this feed were below the detection limits for N.A.A. A summary of the product analyses and feed analysis for the detectable elements is presented in Table 21. Corresponding atomic absorption analyses run by HRI are also presented.

The levels of five of the six elements were reduced as a result of contact with the three different demetallization solids. The level of manganese in the feed would appear to be lower than that in the demetallized products according to the values presented. No explanation for this apparent discrepancy can be given. The relative ability of the catalysts to remove the other metals is activated bauxite < activated clay < two percent Mo/activated bauxite.

Table 19. QUANTITATIVE N.A.A. ANALYSES OF VACUUM RESIDUA

Element	Concentration (ppm)		
	Bachaquero V. B.	Gach Saran V. B.	Tia Juana V. B.
Vanadium	977 ± 200	445 ± 89	662 ± 130
Manganese	0.676 ± 0.140	0.307 ± 0.061	0.056 ± 0.011
Nickel	99 ± 22	111 ± 23	55.8 ± 12.0
Arsenic	0.088 ± 0.019		0.261 ± 0.093
Copper	3.55 ± 0.71	1.76 ± 0.35	
Silver	0.97 ± 0.38		
Sodium	11.7 ± 2.3	4.36 ± 0.87	18.0 ± 3.6
Cobalt	0.59 ± 0.16		0.565 ± 0.130
Chlorine	28.2 ± 5.7	17.2 ± 3.5	
Bromine	0.146 ± 0.044	1.63 ± 0.33	
Iodine		0.69 ± 0.14	
Gallium		0.275 ± 0.071	
Gold	0.0044 ± 0.0012		

Table 20. TRACE ELEMENT ANALYSES

COMPUTER CALCULATED UPPER LIMITS FROM INSTRUMENTAL NEUTRON ACTIVATION ANALYSES OF VACUUM RESIDUA

(Results - Upper Limits Only)

Element	Calculated Upper Limits (Parts Per Million)		
	Bachaquero	Gach Saran	Tia Juana
AG	--------	1.10000	0.43000
AL	34.00000	10.00000	110.00000
AS	--------	0.03800	--------
AU	--------	0.00160	0.00060
BA	0.37000	0.28000	0.30000
BR	--------	--------	0.05700
CD	1.60000	1.30000	0.76000
CE	2.00000	2.00000	0.95000
CL	--------	--------	4.40000
CO	--------	0.55000	--------
CR	3.10000	3.20000	1.30000
CS	0.06600	0.05300	0.03300
CU	--------	--------	0.07400
DY	0.00380	0.00300	0.00210
ER	0.19000	0.16000	0.06800
EU	0.00078	0.00064	0.00030
FE	250.00000	230.00000	110.00000
GA	0.07300	--------	0.05600
GD	1.00000	0.95000	0.63000
GE	1.40000	1.00000	1.20000
HF	0.16000	0.17000	0.06700
HG	0.15000	0.13000	0.08400
HO	0.01400	0.01200	0.00870
I	0.15000	--------	1.20000
IN	0.00078	0.00053	0.00110
IR	0.00240	0.00260	0.00097
K	5.10000	3.30000	3.60000
LA	0.05900	0.04200	0.03700
LU	0.01400	0.01300	0.00610
MG	550.00000	110.00000	2500.00000
MN	--------	--------	--------
MO	0.92000	0.80000	0.48000
NA	-------	--------	--------
NB	570.00000	520.00000	240.00000
ND	0.71000	0.54000	0.44000
NI	--------	--------	--------
OS	0.27000	0.26000	0.13000
PD	0.35000	0.29000	0.22000
PR	0.84000	0.60000	0.61000
PT	0.87000	0.76000	0.45000
RB	8.50000	7.80000	3.60000
RE	0.01100	0.00960	0.00720
RH	1.00000	0.53000	1.20000
RU	1.20000	1.30000	0.53000
SB	0.04300	0.03700	0.01700
SC	0.02200	0.02100	0.00940
SE	2.10000	2.00000	0.82000
SM	0.00420	0.00360	0.00230
SN	3.80000	2.50000	3.50000
SR	0.80000	0.63000	0.40000
TA	0.16000	0.15000	0.07600
TB	0.08200	0.08100	0.03400
TE	0.95000	0.51000	0.93000
TH	0.12000	0.11000	0.04400
TI	670.00000	390.00000	840.00000
TM	1.90000	1.80000	0.90000
U	0.01300	0.00700	0.01800
V	--------	--------	--------
W	0.05600	0.04800	0.03500
Y	29.00000	23.00000	13.00000
YB	0.06800	0.07100	0.02800
ZN	5.30000	4.80000	3.90000
ZR	25.00000	18.00000	17.00000

Above results for 4 data sets.

Table 21. TRACE METAL ANALYSES ON TIA JUANA VACUUM RESIDUUM FEED AND SELECTED DEMETALLIZED PRODUCTS USING NEUTRON ACTIVATION AND ATOMIC ABSORPTION ANALYSES

	Concentration (ppm)							
Product[a] (or Feed)	HRI 2414 (Feed)		185-192-6		185-199-5		184-165-7	
Catalyst Employed	No Catalyst		12 x 20 Mesh Act. Bauxite		12 x 20 Mesh Act. Clay		2% Mo/Act. Bauxite, LX-18	
	N.A.A.	A.A.[b]	N.A.A.	A.A.	N.A.A.	A.A.	N.A.A.	A.A.
Element								
Vanadium	662 ± 130	550	---------	286	---------	266	---------	211
Manganese	0.0559 ± 0.0110	---	0.186 ± 0.001	---	0.149 ± 0.001	---	0.139 ± 0.001	---
Nickel	55.8 ± 12.0	74	---------	64	---------	62	---------	50
Arsenic	0.0261 ± 0.0093	---	0.017 ± 0.003	---	0.010 ± 0.003	---	0.0078 ± 0.0026	---
Sodium	18.0 ± 3.6	---	0.0665 ± 0.008	---	0.133 ± 0.005	---	0.122 ± 0.005	---
Cobalt	0.565 ± 0.130	---	0.18 _ 0.02	---	0.17 ± 0.02	---	0.11 ± 0.02	---

a. Identifying product code: Unit-Run No.-Period No.

b. Analyses run by HRI using atmoic absorption. Value represents an average of several samples and analyses of the Tia Juana vacuum feed.

SECTION V

PROCESS ECONOMICS

The major costs in producing low sulfur fuel oil from high metals residua are related to the cost of the facility necessary to carry out the desulfurization, the amount of hydrogen consumed, and the cost of the catalyst. Summaries have been prepared of the processing costs, including investment requirements, for producing 0.3, 0.5, and 1.0 weight percent sulfur fuel oil from Tia Juana vacuum bottoms, Bachaquero vacuum bottoms, and Gach Saran vacuum bottoms utilizing unpromoted bauxite and the new LX-22 catalyst for the demetallization step.

The data computations for the 0.5 weight percent sulfur fuel oil product case requires almost no amount of extrapolation from the operating conditions utilized in the experimental program. For those cases where 0.3 weight percent sulfur and 1.0 weight percent sulfur fuel oil is produced, some extrapolation of the data is necessary.

Curves have been prepared which show these operating costs, including a 25 percent charge for investment for producing 0.5 weight percent sulfur from the three residua studied as a function of the level of demetallization achieved in the demetallization step and a demetallization catalyst cost of $0.12, $0.16, and $0.20 per pound. The cost calculations are based on 1973 Gulf Coast construction costs and are for a 20,000 barrels per day plant, which is perhaps the minimum size that a refiner would build.

Figure 22 shows that, for Gach Saran vacuum bottoms, there was an optimum demetallization level of 85 percent, which minimizes the overall costs. At this optimum point, the cost is $1.19 per barrel if the demetallization catalyst cost is $0.20 per pound.

With the two Venezuelan feeds, the overall costs of producing the desulfurized fuel oil product decreased as demetallization increased, but it was difficult to achieve more than 69 percent demetallization on Tia Juana vacuum residuum or 73 percent demetallization on Bachaquero vacuum residuum. The reason for this is that the operating severities became too great to confidently predict that long term satisfactory demetallization catalyst life

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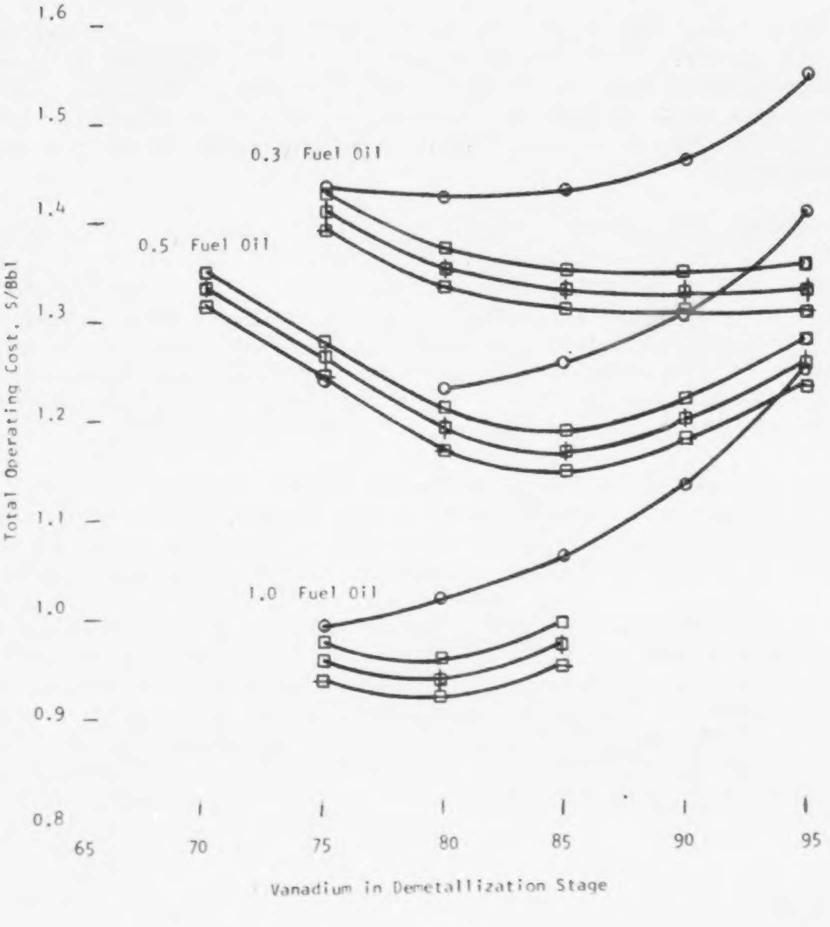
Figure 22. TOTAL OPERATING COST

TWO-STAGE DEMETALLIZATION-DESULFURIZATION OF GACH SARAN VACUUM RESIDUUM

Bases: (1) 20,000 B/D, (2) 1973 Gulf Coast Construction Costs, (3) $0.50/1000 SCF H_2, (4) Capital Charges - 25 of Investment

LEGEND

Symbol	Catalyst Demetallization/Desulfurization	Demetallization Catalyst Cost, $/Lb
○	Activated Bauxite/Beads	0.05
□	LX-22/Beads	0.20
◫	LX-22/Beads	0.16
⊟	LX-22/Beads	0.12



could be achieved. Furthermore, the actual removal of metals from these stocks beyond this level is believed to be unnecessary or of limited economic value since these metal compounds are hard to remove and, therefore, would also be difficult to remove with the desulfurization catalyst. Overall costs for these two feeds are $1.46 and $1.64 per barrel, respectively, and are shown in Figures 23 and 24. The sets of curves for the production of 0.3 percent sulfur fuel oil and 1.0 percent sulfur fuel oil show an additional cost of about $0.40 per barrel of product to produce the 0.3 percent material and a cost of about $0.40 per barrel less to produce the 1.0 percent material. These calculations were made assuming a constant set of demetallization operating conditions for a given level of demetallization with the only variation being the operating conditions of the desulfurization plant.

The overall processing costs are sharply dependent on plant capacity. With this in mind, costs have been prepared for Bachaquero vacuum residuum using $0.20 per pound as the price of the demetallization catalyst and varied plant size between 20,000 and 100,000 barrels per day. As can be seen from Figure 25, raising plant capacity from 20,000 to 100,000 barrels per day reduces the per barrel cost of 0.5 percent sulfur fuel oil from $1.64 to $1.46.

One of the original objectives of the program was to try and reduce the overall hydrogen consumption to produce the desulfurized fuel oil product. Calculations have not been done on all the feeds and product sulfur levels, but for a Bachaquero vacuum residuum case for the production of 0.5 percent sulfur fuel oil, the demetallization step at the optimum level requires 740 SCF per barrel and the desulfurization step requires 360 SCF per barrel for a total of 1100 SCF. With the activated bauxite, the comparable values are 590 SCF per barrel for demetallization and 760 SCF per barrel for desulfurization, making a total of 1350 SCF per barrel. The difference of 250 SCF per barrel is worth on the order of $0.125 per barrel in direct processing cost reductions. The higher hydrogen consumption utilization in the first stage demetallization step with the improved catalyst is due to its having a definite hydrogenation function. Some of the sulfur which is removed with the demetallization step requires the addition of hydrogen. However, since less desulfurization has to be done in the desulfurization stage, the operating requirements are less severe in that stage and the total hydrogen consumed worked out to be less with the new improved catalyst.

The influence on the overall economics of the price of the demetallization catalyst is obviously strong as indicated by Figures 22, 23, and 24. Consultation with a leading catalyst manufacturer

Figure 23. TOTAL OPERATING COST

TWO-STAGE DEMETALLIZATION-DESULFURIZATION OF TIA JUANA VACUUM RESIDUUM

Bases: (1) 20,000 B/D, (2) 1973 Gulf Coast Construction Costs, (3) \$0.50/1000 SCF H_2. (4) Capital Charges - 25% of Investment

LEGEND

	Catalyst	
Symbol	Demetallization/Desulfurization	Demetallization Catalyst Cost, \$/Lb
○	Activated Bauxite	0.05
□	LX-22/Beads	0.20
⌽	LX-22/Beads	0.16
⊖	LX-22/Beads	0.12

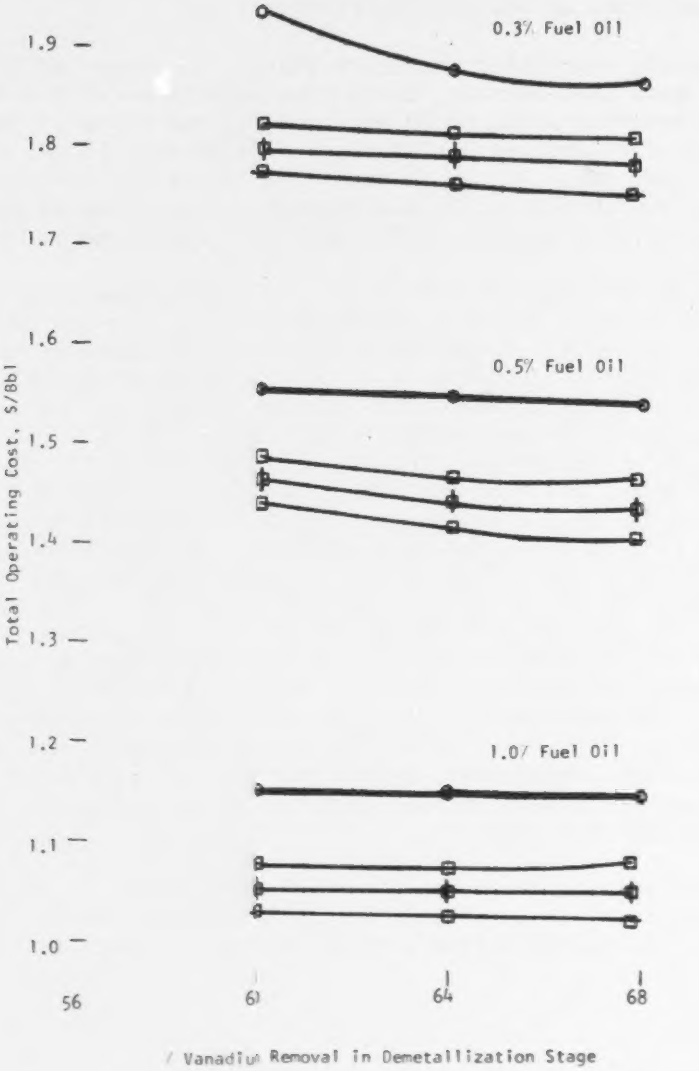


Figure 24. TOTAL OPERATING COST

TWO-STAGE DEMETALLIZATION-DESULFURIZATION OF BACHAQUERO VACUUM RESIDUUM

Bases: (1) 20,000 B/D, (2) 1973 Gulf Coast Construction Costs, (3) $0.50/1000 SCF H_2, (4) Capital Charges - 25% of Investment

LEGEND

Symbol	Catalyst Demetallization/Desulfurization	Demetallization Catalyst Cost, $/Lb
○	Activated Bauxite/Beads	0.05
□	LX-22/Beads	0.20
◫	LX-22/Beads	0.16
⊟	LX-22/Beads	0.12

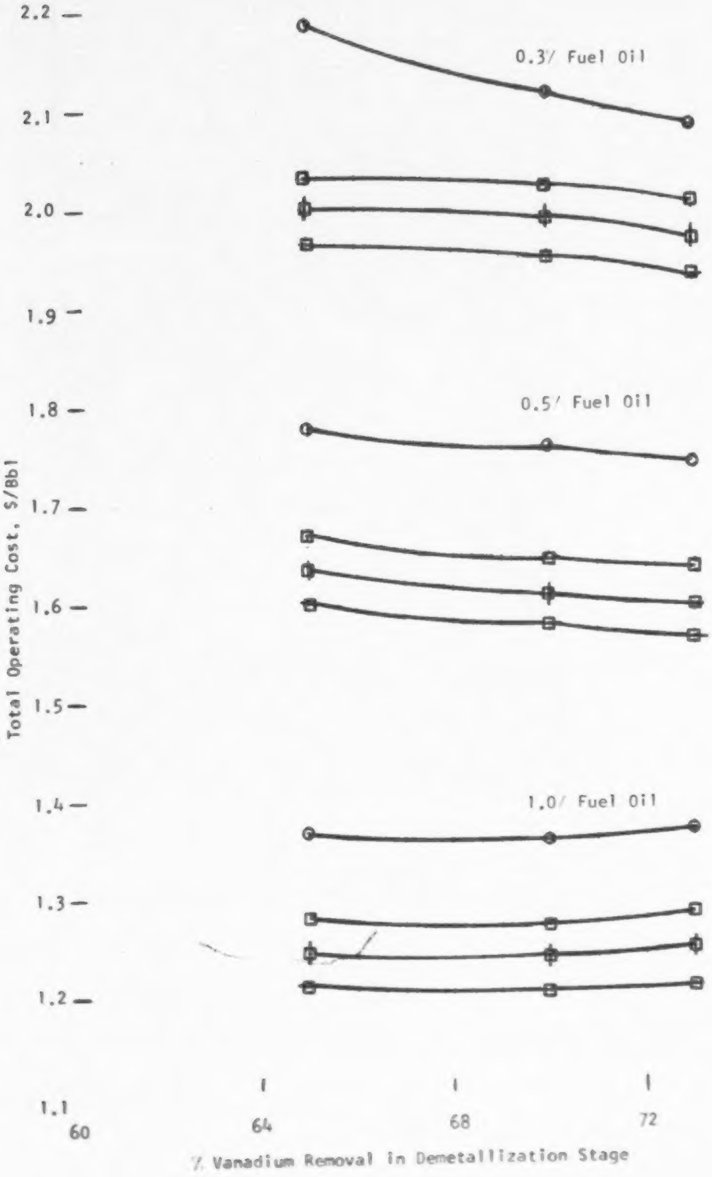
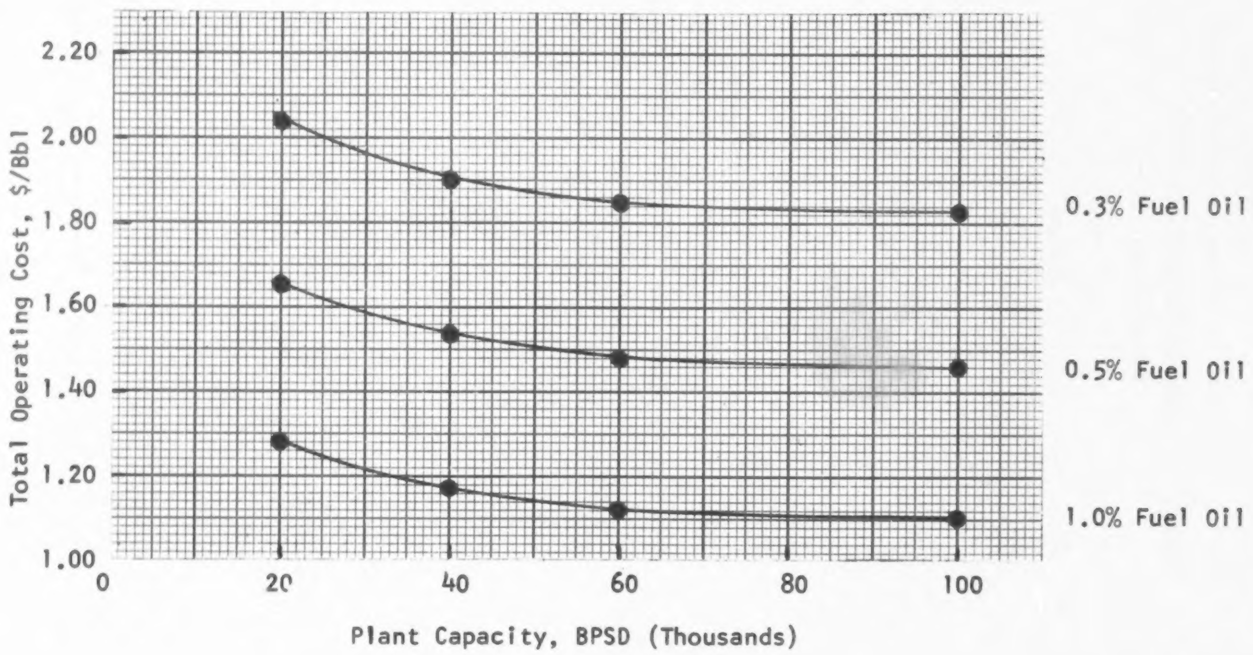


Figure 25. OVERALL COSTS FOR PRODUCING LOW SULFUR FUEL OIL FROM BACHAQUERO VACUUM RESIDUUM



indicated that the costs of impregnation of the cheapest support are on the order of \$0.10 per pound minimum regardless of the material to be impregnated. The activated bauxite used in this work sells in massive quantities for on the order of about \$0.05 per pound. The value of the molybdenum and other chemicals used in the preparation of the catalyst are on the order of \$0.04 per pound. Therefore, the cost of the finished catalyst will be of the order of \$0.20 per pound. If some economies in production can be obtained as the result of future development work and/or the amount of molybdenum necessary to achieve the desired result can be lowered, it is conceivable that the cost of the finished demetallization catalyst can come down. Curves have been presented in all cases for alternate prices of \$0.12 and \$0.16 per pound.

Estimates of the overall yield structure and properties of the various fractions are given in Tables 22, 23 and 24 for the production of 400°F+ fuel oil containing 1.0, 0.5, and 0.3 weight percent sulfur from Gach Saran, Tia Juana, and Bachaquero vacuum residua.

Table 22. ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES

CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF GACH SARAN VACUUM RESIDUUM

400°F+ Fuel Oil Sulfur, W/	1.0				0.5				0.3			
YIELDS												
	W/	V/	°API	/S	W/	V/	°API	/S	W/	V/	°API	/S
H_2S & NH_3	2.7				3.4				3.6			
C_1-C_3	0.9				1.1				1.5			
C_4-400°F	3.9	5.5	63	< 0.07	5.0	7.0	63	<0.07	6.7	9.5	63	< 0.07
400-650°F	7.9	9.6	35	0.10	10.3	12.5	35	< 0.07	13.4	16.2	35	<0.07
650-975°F	25.8	28.4	20	0.26	27.2	30.0	20	0.10	28.1	30.9	20	<0.07
975°F+	59.7	61.0	9.2	1.43	54.3	55.8	10	0.78	48.1	49.8	11	0.50
400°F+	93.4	99.0	14.3	1.0	91.8	98.3	15.8	0.5	89.6	96.9	17.3	0.3
TOTAL	100.9	104.5	16.3	0.96	101.3	105.3	18.2	0.47	101.4	106.4	20.5	0.28

Table 23. ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES

CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF TIA JUANA VACUUM RESIDUUM

400°F+ Fuel Oil Sulfur, W%	1.0				0.5				0.3			
YIELDS	W%	V%	°API	%S	W%	V%	°API	%S	W%	V%	°API	%S
H_2S & NH_3	2.3				2.9				3.2			
C_1-C_3	1.1				1.6				2.0			
C_4-400°F	4.7	6.5	62	<0.07	6.5	9.0	62	<0.07	7.9	11.0	62	<0.07
400-650°F	9.8	11.7	34	0.10	12.7	15.1	34	<0.07	14.8	17.8	35	<0.07
650-975°F	25.2	27.5	20	0.27	26.5	29.1	21	0.10	27.3	30.0	21	<0.07
975°F+	57.9	58.9	10	1.46	51.1	52.4	11	0.81	46.2	47.7	12	0.53
400°F+	92.9	98.1	15.3	1.0	90.3	96.6	17.2	0.50	88.3	95.5	18.8	0.30
TOTAL	101.0	104.6	17.4	0.95	101.3	105.6	20.1	0.46	101.4	106.5	22.4	0.28

Table 24. ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES

CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF BACHAQUERO VACUUM RESIDUUM

400°F+ Fuel Oil Sulfur, W	1.0				0.5				0.3			
YIELDS												
	W/	V/	°API	/S	W/	V/	°API	/S	W/	V/	°API	/S
H_2S & NH_3	3.0				3.6				3.9			
C_1-C_3	1.1				1.6				2.0			
C_4-400°F	4.3	6.0	63	<0.07	6.0	8.5	63	<0.07	7.2	10.2	63	<0.07
400-650°F	9.7	11.7	35	0.10	12.4	15.0	35	<0.07	14.5	17.5	35	<0.07
650-975°F	28.7	31.6	20	0.28	29.9	33.1	21	0.11	30.5	33.8	21	<0.07
975°F+	54.5	55.6	9	1.53	48.1	49.4	10	0.85	43.7	45.3	11.4	0.55
400°F+	92.9	98.9	15.2	1.0	90.4	97.5	17.1	0.50	88.7	96.6	18.6	0.3
TOTAL	101.3	104.9	17.2	0.95	101.6	106.0	20.0	0.46	101.8	106.8	21.9	0.28

SECTION VI

APPENDICES

		Page No.
A.	Detailed Analysis of Demetallization Patents	85
B.	Outline of Detailed Procedures for Catalyst Preparation	99
C.	Summary of Catalyst Screening Runs	109
D.	Summary of Demetallization Runs	117
E.	Summary of Desulfurization Runs	123
F.	Operating Conditions, Yields, and Product Properties	129
G.	Conversion Table	143
H.	Glossary	147

APPENDIX A

DETAILED ANALYSIS OF DEMETALLIZATION PATENTS

U.S. Patent 3,725,251

A multistage process for the hydrodesulfurization of high metals (Ni and V) content petroleum residua wherein the first reaction zone is an ebulated bed contacting system using a powdered (40 x 325 mesh) demetallization catalyst to effect improved demetallization and thereby lower catalyst deactivation in subsequent desulfurization stages. Enhanced demetallization is shown to be effected through the reduction in the particle size of an alumina or silica and alumina catalyst promoted with metals and their compounds from Group VI-B (C_r, Mo, W) and Group VIII (Fe, Co, Ni primarily) of the Periodic Table. Furthermore, improved demetallization was further effected by incorporating access channels comprising from 20 to 80 percent of the total pore volume into the structure of the demetallization catalyst. These access channels are interstitially spaced throughout the microporous matrix and have diameters greater than 100 angstroms. Furthermore, the size of these access pores should have a broad distribution such that 10 to 40 percent of the total pore volume is in pores about 1,000 angstroms diameter and another 10 to 40 percent in pores of diameter between 100 and 1,000 angstroms in diameter.

U.S. Patent 3,716,479

The patent describes a process whereby petroleum residua are contacted with a demetallization catalyst prepared from naturally occurring underwater deposits known as manganese nodules. In addition to manganese, these catalysts also contain varying amounts of other metals, including iron, cobalt, nickel, and copper. The catalysts are prepared from the manganese nodules by simply crushing to size, washing (in the case of the ocean nodules to remove sodium chloride), and drying.

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These high surface area catalysts (100-250 M^2/g) can be further modified by leaching out certain of the metals or sulfiding the metals contained in the nodules. High levels of nickel and vanadium removal are reported at moderate hydrogenation conditions considering the type of processing involved. A significant advantage of the manganese nodule demetallization catalyst is their low activity for the hydrogenation of aromatic rings, thereby effecting low hydrogen consumption during demetallization. No details regarding porous structure were given.

U.S. Patent 3,712,861

This patent relates to a process in which petroleum residua is contacted with a porous alumina which contains sulfides of the Group VI and Group VIII metals. The aluminas used are large pore adsorbents with average pore diameters greater than 100 angstroms and preferably less than 100 M^2/g. This is to permit the relatively unrestricted movement of the large metal containing molecules into the catalyst and to allow relatively high metal deposition before deactivation would occur. The demetallization catalyst is used to effect a substantial metals removal in the first stage of a two-stage hydrogenation operation.

U.S. Patent 3,696,027

This patent describes a process where a metals contaminated heavy petroleum oil is treated under hydroconverting conditions by successive contact with fixed beds of (a) macroporous catalyst particles having a high metals capacity and low desulfurization activity, (b) macroporous catalysts of moderate desulfurization activity, and (c) catalyst with a high desulfurization activity. In this case, the term macropore refers to pores, channels, or openings in the catalyst particle greater than 500 angstroms in diameter. The first catalyst zone has at least 30 volume percent of the catalyst pore volume in the macropore region, the second between five and 40 volume percent and the third less than five volume percent. This "graded catalyst" arrangement takes advantage of the macroporous catalysts' enhanced capacity for metals removal. The composition of the catalysts employed was nickel-molybdenum on alumina-silica supports.

U.S. Patent 3,691,063

The patent describes a process in which petroleum residua to be hydrocracked is first treated in a guard case containing demetallization catalyst. The catalyst is said to be a sulfided form of nickel, nickel-tungsten, nickel-molybdenum, cobalt, cobalt-tungsten, or cobalt-molybdenum supported on silica-alumina or alumina. The guard case catalyst is regenerated using oxygen and steam which removes coke deposits.

U.S. Patent 3,617,481

This patent describes a novel demetallization process in which the contact solid is prepared by coking the heavy, high metals fraction of petroleum residua. Mild deactivation of the coke with air and steam is employed to increase the porosity and expose nickel and vanadium which in turn act as demetallization catalysts. Alternately, the activated coke can also be impregnated with compounds of cobalt, molybdenum, and additional quantities of nickel and vanadium to further enhance demetallization activity. Alkali metals carbonates may be employed to promote the gasification reaction and produce a high surface area coke which is said to be a more active metals removal catalyst.

U.S. Patent 3,607,725

This patent describes a process in which metals in crude or residua are removed using a multibed reactor with descending catalyst and ascending feed, i.e., a series of fluidized beds. The demetallization catalyst is only described as a nickel-molybdenum on alumina type. Use of this relatively inexpensive demetallization catalyst in the multibed demetallization reactor system ahead of a hydrocracker protects the relatively expensive, high activity catalyst from deactivation and allows the use of lower pressure than would normally be the case without prior demetallization.

U.S. Patent 3,576,737

This patent describes a process for the demetallization of atmospheric residua in which the demetallization catalyst is 0.5 to 10 weight percent vanadium on a macroporous support. The support should have an average pore diameter which is greater than 300 angstroms and preferably greater than 500 angstroms. The preferred catalyst is a macroporous 8 x 14 mesh alundum support with a surface area of 23 M^2/g and an average pore diameter of 840 angstroms onto which vanadium is impregnated from solution. Vanadium pentoxide, V_2O_5, dissolved in oxalic acid was used as the impregnant. However, large pore diameter charcoal, alumina, silica, and alumina silica particles may also be used.

Demetallization activity was found to proceed in this order: vanadium on alundum <high surface, commercial nickel molybdenum hydrotreating catalyst <<alundum with no vanadium. Although an autocatalytic effect resulting from the deposition of organometallic vanadium onto the unpromoted alundum was noted, it was stated that, for most feeds, this effect was not sufficent by itself to afford satisfactory contaminant metal removal rates.

U.S. Patent 3,563,887

This patent disclosed a process for the hydrodesulfurization of petroleum fraction containing the asphaltene fraction and, consequently, the large majority of the metallorganic contaminants found in the crude. This is accomplished at unexpectedly low temperatures by utilizing a supported Group VI and Group VIII metal-containing catalyst of a size (1/20"-1/40") substantially smaller than had previously been used in a fixed bed reactor. Although the patent is primarily concerned with the proper apportioning of the catalyst between the guard chamber and the main reactor and the frequency of renewal of the guard chamber, it is concerned with metals removal in that the small catalyst particle size enables the catalyst in the guard chamber to do an effective job of metals removal while maintaining the desulfurization activity of the bulk of the catalyst in the main reactor. Thus, the importance of a small demetallization catalyst particle size in obtaining both the maximum demetallization rate and metals deposition capacity is shown.

U.S. Patent 3,553,106

This patent discloses a process for the hydrogenative removal of vanadium from both crudes and atmospheric residua using a preferred vanadium oxide catalyst on activated alumina. This catalyst is claimed to have both higher activity and higher vanadium removal capacity than the more expensive nickel-cobalt-molybdenum on alumina hydrogenation catalysts. Preparation of the catalyst is achieved through impregnation of the alumina support with a non-oily solution of vanadium compounds including vanadium oxalate, vanadyl acetyl, acetonate, and the like. Vanadium levels of from 0.5 to 5.0 weight percent are the preferred loadings with one to about three weight percent being especially preferred. After drying the impregnated support, an air calcination is carried out to decompose the vanadium compound and form vanadium oxide in an active state. Although a wide range of aluminas having surface areas between 40 and about 400 M^2/g may be employed, an especially preferred activated alumina is one comprising major amounts of gamma and eta aluminas. Furthermore, this type of vanadium removal catalyst was found to be more active than is a catalyst resulting from the in situ deposition of vanadium from the oil onto an initially vanadium-free alumina.

U.S. Patent 3,530,066

This patent describes an improved process to eliminate asphaltenes and metallic contaminants with a catalytic solid having a plurality of pores between 1,000 and 50,000 angstroms in diameter. Further, these pores are present in a pore volume of 0.05-0.9 cc/g of the solid. The majority of this porosity is preferred to be in the range of 2,000 to 35,000 angstroms. This type of porosity is obtained by mixing refractory particles of 20-500 microns with 1-15 weight percent of alumina hydrogel, followed by molding, drying, and calcination. The refractory particles chosen from the group consisting of bauxite, magnetite, laterite, diatomaceous earth, clays, ochre, and bentomite are to contain unspecified amounts of at least one member selected from the group consisting of iron, cobalt, nickel, tungsten, chromium, molybdenum, and vanadium. The purpose of incorporating this extensive macroporosity into the catalyst is mainly to overcome the rapid pore blockage accompanying the laydown of both coke and asphaltene products which accompany the treatment of heavy petroleum oils with conventional hydrotreating catalysts.

U.S. Patent 3,383,301

This patent discloses a process for catalytically hydrodesulfurizing a sulfur-containing petroleum oil containing residual components and organometallic components normally capable of poisoning catalysts due to the buildup of both deposited metals and coke in or at the mouths of the pores. To overcome the poisoning effects of both coke and metals deposition and consequently maintain both high desulfurization and demetallization capabilities, an alumina based catalyst containing at least one hydrogenation component from the metals of Group VI-B and Group VIII of the Periodic Table having a relatively uniform, wide distribution of pores in the range of 0 to 300 angstroms in radius is employed. More specifically, the catalyst should not have more than 15 percent of the volume of pores having a radius in the range of 0 to 300 angstroms in any 10 angstrom unit increment, starting at 0 angstrom, while having at least 10 percent in the 0 to 30 angstrom range, at least 15 percent in the 30 to 70 angstrom range, and at least 30 percent in the 70 to 120 angstrom range. This catalyst also has a minimum surface area of 100 M^2/g.

U.S. Patent 3,362,901

This patent describes a two-stage hydrogenation process in which a catalyst is employed in the first stage which causes the asphaltenes in a petroleum residua to agglomerate after which the agglomerates are removed before further hydrogenation of the oil is carried out in the subsequent stage. In the process of removing the agglomerated asphaltenes, a substantial portion of the feed metals is accomplished. The first stage catalyst can either be an inert particulate, such as tabular alumina, extruded alumina, or a low activity catalyst. Alternatively, the first stage catalyst can be a support such as alumina, silica, silica alumina, magnesia, titania, etc., promoted with about 0.5 to three percent of a metal in Group VII of the Periodic Table in combination with two to 15 percent of a Group VI-B metal. Obviously, the operating condition must be such that the metal-containing asphaltene agglomerates rather than deposits to a significant degree on the first stage catalyst itself as would normally be the case.

U.S. Patent 3,297,589

This patent is directed toward the preparation of a novel hydrorefining catalyst which is used in processes for the removal of organometallic contaminants from residual petroleum fractions. The carrier used for the preparation of the catalyst is a refractory inorganic oxide, preferably a composite of alumina and silica, with alumina being the greater proportion. However, other refractory inorganic oxides, e.g., zirconia, magnesia, titania, boria, strontia, hafia, and mixtures of two or more, could be employed in conjunction with alumina. Pore size distribution and surface area are described in such broad terms as not to yield any specific information in these areas.

After drying and calcination to remove the physically-bound, and a large portion of the chemically-bound, water the carrier is impregnated with an aqueous or nonaqueous decomposable vanadium compound such as vanadium trichloride, but not limited to this species, such that the final catalyst contains between 1.0 and 30.0 percent by weight of vanadium as the metal. After drying in such a way as not to decompose the vanadium compounds, if other than vanadium trichloride, the catalyst is treated with sulfur monochloride, sulfur dichloride, or mixtures of these two compounds with the results that vanadium trichloride is dispersed throughout the catalyst support in a complex with components in the carrier material. After a further calcination at 150°F to 500°F, the catalyst is used to remove a substantial fraction of both the metal and asphaltenic contaminants. Regeneration is achieved by burning off deposited coke and again treating with sulfur mono- or dichloride.

U.S. Patent 3,227,645

This patent describes a catalytic hydrogenation process for the removal of metal contaminants from hydrocarbon feeds prior to hydrocracking or catalytic cracking. The demetallization catalyst is composed of one or more of the oxides, sulfides, or other compounds of metals of Group VI and/or Group VIII of the Periodic Table alone or supported on a carrier. Typically, the carrier is a refractory oxide, such as alumia, silica, or silica alumina. However, charcoal and other "inert" materials may also be used.

U.S. Patent 3,180,820

This patent discloses a catalytic hydrogenation process for removing metals contaminants from a variety of hydrocarbon oil feeds. The catalyst is described as comprising a metallic component having hydrogenation activity which may be employed in the unsupported state or in a supported form. The supports are described as refractory inorganic oxide materials having a medium to high surface area and a well developed pore structure. Suitable metal components include metals of Groups V-B, VI-B, and VIII of the Periodic Table.

U.S. Patent 2,987,470

This patent relates to an improved hydrogenation process for the removal of metallic impurities from hydrocarbon oils in an ebullated bed reactor system, i.e., a fluidized bed consisting of three phases; gas, liquid, and solid particulate in intimate contact. A particle size of about three to 20 mesh can be fluidized in this type of system without carryover of the catalyst. The particulate contact material onto which the metal contaminants are deposited may be bauxite, alumina, sand, coke, beryl, silicon carbide, magnesia, and iron ore. No specific requirements as to physical or chemical structure of these contact solids are mentioned. Alumina and bauxite appear to be the preferred solids.

U.S. Patent 2,970,957

This patent describes a catalytic hydrogenation process for the removal of vanadium and/or sodium from petroleum residua using a regenerated cobalt molybdate hydrotreating catalyst. Although the type of catalyst suffers a permanent loss in activity for desulfurization due to the presence of deposited metal contaminants, the inventors found that the activity for vanadium and sodium removal does not decline at the same rate. Therefore, the regenerated catalyst can be used in the process long after the effectiveness for desulfurization has fallen below an economical level. Even after prolonged use and nine regenerations (i.e., coke burn-off), this type of catalyst is superior to fresh activated bauxite for vanadium removal.

U.S. Patent 2,945,803

This patent describes a hydrogen treatment process in which demetallization catalysts composed of oxides or sulfides of the Group VI metals, such as molybdenum, tungsten, vanadium, etc., are used alone or in combination with the oxides or sulfides of the iron group metals such as nickel, cobalt, or iron. The catalysts are composited with a carrier such as activated alumina, alumina, silica, "Alfrax" or kieselguhr. One of the major considerations in the distillation of the crude is that the residue fed to the demetallization stage of the process not have a sulfur-to-metals ratio less than 200 or else this treatment will not effectively remove the metals contaminants. This would appear to indicate some difficulty when a vacuum residuum is demetallized using the general type of hydrotreating catalysts just described.

U.S. Patent 2,891,005

This describes a process in which residual oils are hydrogenated in the presence of a cobalt molybdenum on alumina catalyst in such a manner that microcoke particles, containing much of the metal contaminants presented in the feed, are formed. Thus, the metals contaminants are reduced by subsequent removal of these microcoke particles rather than by deposition on the catalyst itself.

U.S. Patent 2,891,004

This describes a process for removing metals contaminants from petroleum by treating the feed with boron compounds either supported or unsupported, such as boron oxide or boric acid. The boron compounds form complexes with the feed metals which can be separated from the oil through settling of the complex itself or, in the case of the supported boron compounds, through a separation of the solid support.

U.S. Patent 2,769,758

This patent describes a process for the removal of sodium and vanadium contaminants from petroleum hydrocarbon feeds prior to desulfurization. The porous contacting agent employed in the metals removal stages is bauxite. The sodium removal is accomplished through a nonhydrogenative step prior to removal of vanadium in a subsequent hydrogenative step. This is accomplished in a single bed of bauxite by admitting recycle hydrogen at a point in the bed calculated to afford the optimum space velocities for both sodium and vanadium removal.

U.S. Patent 2,764,758

This patent disclosed still another catalytic hydrogenation process for the removal of metallic contaminants from petroleum feeds. This patent is directed to the removal of both vanadium and/or sodium by contacting petroleum or petroleum products with a catalyst composed of five to 15 weight percent ferric oxide on alumina.

U.S. Patent 2,730,487

This patent is essentially identical to U.S. 2,764,758 except that the demetallization catalyst is composed of one to ten weight percent of TiO_2 on alumina. In this case, the TiO_2

alumina catalyst has a higher demetallization activity than does ferric oxide/alumina catalyst cited in U.S. 2,764,758.

U.S. Patent 2,687,985

This patent complements U.S. 2,769,758 in that it effects the removal of both sodium and vanadium from residual oils at conditions which are optimum for the nonhydrogenative removal of sodium and for the subsequent removal of vanadium prior to hydrodesulfurization.

APPENDIX B

OUTLINE OF DETAILED PROCEDURES FOR CATALYST PREPARATION

Catalyst LX-1: Activated Bauxite Impregnated with 5% Fe

Five hundred ml of 12 x 20 mesh bauxite was heated in air at 950°F for 16 hours, then cooled and weighed. The weight was 448 grams. On a separate sample of support, it was determined that 62 ml of water covered 100 grams of support.

The impregnating solution was prepared by adding 181 grams Fe $(NO_3)_3.9H_2O$, equivalent to 26 grams Fe, to water in a graduated beaker. After dissolving, additional water was added so that the total water was 310 ml.

The support was placed in a Pyrex tray, 8 x 12 x 2 inches, and the solution was poured evenly over the support. The tray was heated on a hot plate with continuous stirring. Near the end of the heating, which took about two hours, continuous agitation with a wide flat spatula was required to keep the catalyst from agglomerating.

The catalyst was transferred to a 600 ml porcelain evaporating dish and placed in a muffle furnace held at 950°F ± 25°F having a small air bleed. After 16 hours, the catalyst was removed from the furnace, covered with a watch glass, and allowed to cool to approximately room temperature. It was then transferred to a glass jar and tightly stoppered.

A total of 488 grams of catalyst was recovered.

Catalyst LX-2: Activated Bauxite Impregnated with 5% Co

The same amount of support was prepared by the method used for LX-1. The impregnating solution was prepared by dissolving 128 grams $Co(NO_3)_2.6H_2O$, equivalent to 26 grams of Co, in water and diluting to a final volume of 310 ml. The impregnation,

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drying, and calcining were the same as used for LX-1. A total of 488 grams of catalyst was recovered.

Catalyst LX-3: Activated Bauxite Impregnated with 5% V

A total of 500 ml (447 grams) of support was prepared by the same method used for LX-1. The impregnating solution was prepared by suspending 54 grams NH_4VO_3, equivalent to 23.5 grams of V, in 275 ml water. The mixture was heated to about 125°F and a solution of 18.5 grams of NaOH in 35 ml of water was added slowly while stirring. The impregnation, drying, and calcining were the same as used for LX-1. A total of 496.4 grams of catalyst was recovered.

Catalyst LX-4: Activated Bauxite Impregnated with 5% Mo

A total of 500 ml (448 grams) of support was prepared by the same method used for LX-1. The impregnating solution was prepared by heating 310 ml of concentrated NH_4OH to about 120°F while slowly adding 35.6 grams of MoO_3, equivalent to 23.6 grams of Mo, and stirring constantly. The impregnation, drying, and calcining were the same as used for LX-1. A total of 483.2 grams of catalyst was recovered.

Catalyst LX-5: Activated Bauxite Impregnated with 5% V

A total of 500 ml (440 grams) of support was prepared by the same method as used for LX-1. Then 141 grams of oxalic acid was dissolved in water and diluted to 310 ml. This solution was heated to 140°F and 42 grams of V_2O_5, equivalent to 23.5 grams of V, was slowly added with stirring until dissolved. The impregnation, drying, and calcining were the same as used for LX-1. A total of 471.8 grams of catalyst was recovered.

Catalyst LX-6: Activated Bauxite Impregnated with 5% HPO_3

A total of 500 ml (450.4 grams) of support was prepared by the same method used for LX-1. Then 34.2 grams H_3PO_4 (85%), equivalent to 23.7 grams of HPO_3, was dissolved in water and diluted to 310 ml. This solution was poured slowly over the support and dried on a hot plate with stirring. Calcination was carried out at 650°F for 16 hours. A total of 474.6 grams of catalyst was recovered.

Catalyst LX-7: Activated Bauxite Impregnated with 7.5% Ni

A total of 500 ml (450.8 grams) of support was prepared by the same method used for LX-1. Then 182 grams $Ni(NO_3)_2.6H_2O$, equivalent to 23.7 grams of Ni, was dissolved in water and diluted to 310 ml. The impregnation, drying, and calcining were the same as used for LX-1. A total of 398.4 grams of catalyst was recovered.

Catalyst LX-8: Activated Bauxite Impregnated with 5% Cr

A total of 500 ml (456.3 grams) of support was prepared as in LX-1. Then 185 grams $Cr(NO_3)_3.9H_2O$, equivalent to 24.0 grams of Cr, was dissolved in water and diluted to 310 ml. The impregnation, drying, and calcining were the same as used for LX-1. A total of 492.9 grams of catalyst was recovered.

Catalyst LX-9: Activated Bauxite Impregnated with 10% Fe

A total of 500 ml (450 grams) of support was prepared by the same method used for LX-1. Then 362 grams $Fe(NO_3)_3.9H_2O$, equivalent to 50 grams of Fe, was dissolved in water and diluted to 310 ml. The impregnation, drying, and calcining were the same as used for LX-1. A total of 526.1 grams of catalyst was recovered.

Catalyst LX-11: Activated Bauxite with Low SiO_2 Impregnated with 5% Fe

A total of 500 ml (451.1 grams) of support was prepared in the same manner as LX-1. Then 171.4 grams $Fe(NO_3)_3.9H_2O$, equivalent to 23.7 grams of Fe, was dissolved in water and diluted to 310 ml. The impregnation, drying, and calcining were the same as used for LX-1. A total of 483.7 grams of catalyst was recovered.

Catalyst LX-12: Macroporous Alumina Impregnated with 5% Fe

The alumina was crushed in a mortar and sized to 12 x 20 mesh. A total of 248 ml (185 grams) of the support was prepared and it was calcined at 950°F for 16 hours. Then 70 grams $Fe(NO_3)_3.9H_2O$, equivalent to 9.7 grams of Fe, was dissolved in water and diluted to 155 ml. Impregnation, drying, and calcining were the same as used for LX-1. A total of 199 grams of catalyst was recovered.

Catalyst LX-13: Activated Bauxite Impregnated with 1.5% Co and 5% Mo

A total of 500 ml (450 grams) of support was prepared by the same procedure used for LX-1. Then 36.2 grams of MoO_3, equivalent to 24.1 grams of Mo, were dissolved in 155 ml of hot NH_4OH and diluted with water to 310 ml. This solution was poured over the support which was then dried on a hot plate with stirring. Then 35.6 grams $Co(NO_3)_2.6H_2O$, equivalent to 7.2 grams of Co, were dissolved in water and diluted to 310 ml. This solution was poured over the Mo-impregnated catalyst, which was then dried on a hot plate with stirring, transferred to a porcelain evaporating dish and calcined in a muffle furnace held at 950°F for 16 hours. A total of 499 grams of catalyst was recovered.

Catalyst LX-14: Macroporous Alumina Impregnated with 5% Mo

The alumina support, totaling 250 ml (186.2 grams), was prepared in the same manner as LX-1. Then 14.7 grams of MoO_3, equivalent to 9.8 grams of Mo, was dissolved in 85 ml of hot NH_4OH and diluted to 175 ml with water. Impregnation, drying, and calcining were done in the same manner as used for LX-1. A total of 202.9 grams of catalyst was recovered.

Catalyst LX-15: Activated Attapulgus Clay Impregnated with 9.5% Mo

The clay was ground in a mortar and 500 ml (263.5 grams) of 12 x 20 mesh material was recovered. It was then calcined at 950°F for 16 hours. Then 41.6 grams of MoO_3, equivalent to 27.7 grams of Mo, was dissolved in 150 ml of hot NH_4OH and diluted to 350 ml with water. Impregnation, drying, and calcining were the same as used for LX-1. A total of 298 grams of catalyst was recovered.

Catalyst LX-16: Activated Carbon Impregnated with 11% Mo

The support was crushed and 500 ml (207 grams) of 12 x 20 mesh material was recovered. It was then calcined at 650°F for 16 hours. Then 38.5 grams of MoO_3, equivalent to 25.6 grams of Mo, was dissolved in 150 ml of hot NH_4OH and diluted to 350 ml with water. The impregnation and drying were the same as used for LX-1, but the calcining was done at 650°F for two hours. Some carbon was burned off as evidenced by a white ash on top of the catalyst. A total of 239.5 grams of catalyst was recovered.

Catalyst LX-17: Low Surface Area Alumina Impregnated with 3.8% Mo

The support, totaling 250 ml (337.1 grams), was prepared in the same manner used for LX-1. Then 20 grams of MoO_3, equivalent to 13.3 grams of Mo, was dissolved in 75 ml of hot NH_4OH

diluted to 175 ml with water. The impregnation, drying, and calcining were done in the same manner as in LX-1. A total of 355.7 grams of catalyst was recovered.

Catalyst LX-18: Activated Bauxite Impregnated with 2% Mo

A total of 500 ml (455.5 grams) of support was prepared in the same manner as LX-1. Then 14 grams of MoO_3, equivalent to 9.3 grams of Mo, was dissolved in 75 ml of hot NH_4OH and diluted to 310 ml with water. Impregnation, drying, and calcining were done in the same manner as LX-1. A total of 471.8 grams of catalyst was recovered.

Catalyst LX-19: High Porosity Alumina Impregnated with 8.9% Mo

A total of 300 ml (165.4 grams) of support was prepared in the same manner as LX-1. Then 24.3 grams of MoO_3, equivalent to 16.2 grams of Mo, was dissolved in 75 ml of hot NH_4OH and diluted to 210 ml with water. Impregnation, drying, and calcining were done in the same manner as LX-1. A total of 188.1 grams of catalyst was recovered.

Catalyst LX-20: Activated Attapulgus Clay Impregnated with 2% Mo

A total of 500 ml (263.2 grams) of support was prepared by crushing in a mortar and separating out the 12 x 20 mesh fraction. The remainder of the treatment was the same as used for LX-1. The 8.1 grams of MoO_3, equivalent to 5.4 grams of Mo, was dissolved in 75 ml of hot NH_4OH and diluted to 350 ml with water. Impregnation, drying, and calcining were done in the same manner as used for LX-1. A total of 268 grams of catalyst was recovered.

Catalyst LX-21: Activated Bauxite Impregnated with 1% Mo

A total of 500 ml (456.9 grams) of support was prepared in the same manner as used for LX-1. Then 6.9 grams of MoO_3, equivalent to 4.6 grams of Mo, was dissolved in hot NH_4OH and diluted to 350 ml with water. Impregnation, drying, and calcining were done in the same manner as for LX-1. A total of 460.5 grams of catalyst was recovered.

Catalyst LX-22: Activated Bauxite Impregnated with 2% Mo

A total of 500 ml (478.4 grams) of 20 x 50 mesh support was prepared in the same manner as LX-1. Then 14.7 grams of MoO_3, equivalent to 9.8 grams of No, was dissolved in 50 ml of hot NH_4OH and diluted to 350 ml with water. Impregnation, drying, and calcining were done in the same manner as used for LX-1. A total of 488.7 grams of catalyst was recovered.

Catalyst LX-23: Activated Bauxite Impregnated with 1% Zn

A total of 500 ml (458.9 grams) of support was prepared in the same manner used for LX-1. Then 20.9 grams of $Zn(NO_3)_2.6H_2O$, equivalent to 4.6 grams of Zn, was dissolved in water and diluted to 350 ml. Impregnation, drying, and calcining procedures were the same as used for LX-1. A total of 462.6 grams of catalyst was recovered.

Catalyst LX-24: Activated Bauxite Impregnated with 0.5% Mo

A total of 500 ml (459.9 grams) of support was prepared in the same manner used for LX-1. Then 3.45 grams of MoO_3, equivalent to 2.3 grams of Mo, was dissolved in 50 ml of hot NH_4OH and diluted to 350 ml with water. Impregnation, drying, and calcining procedures were the same as used for LX-1. A total of 463.5 grams of catalyst was recovered.

Catalyst LX-25: Activated Bauxite Impregnated with 0.3% Ni and 1% Mo

A total of 500 ml (452 grams) of support was prepared in the same manner as used for LX-1. Then 6.9 grams of MoO_3, equivalent to 4.6 grams of Mo, was dissolved in 50 ml of hot NH_4OH and diluted to 200 ml with water. Following this step, 6.9 grams of $Ni(NO_3)_2.6H_2O$, equivalent to 1.4 grams of Ni, was dissolved in water and diluted to 150 ml. The two were combined and the support was impregnated, dried, and calcined in the same manner that was used for LX-1. A total of 457.2 grams of catalyst was recovered.

Catalyst LX-26: Activated Bauxite Impregnated with 0.5% Mo

A total of 500 ml (502.6 grams) of 20 x 50 mesh support was prepared in the same manner as used for LX-1. Then 3.75 grams of MoO_3, equivalent to 2.5 grams of Mo, was dissolved in 50 ml of hot NH_4OH and diluted to 350 ml with water. Impregnating, drying, and calcining procedures were the same as used for LX-1. A total of 499 grams of catalyst was recovered.

Catalyst LX-27: Activated Bauxite Impregnated with 1% Mn

A total of 500 ml (498.5 grams) of 20 x 50 mesh support was prepared in the same manner that was used for LX-1. Then 32.1 grams of a 50.7% aqueous solution of $Mn(NO_3)_2$, equivalent to five grams of Mn, was diluted to 350 ml with water. Impregnating, drying, and calcining procedures were the same as used for LX-1. A total of 499 grams of catalyst was recovered.

APPENDIX C

SUMMARY OF CATALYST SCREENING RUNS

Table C-1. SUMMARY OF CATALYST SCREENING RUNS

(Feed: Tia Juana Vacuum Bottoms)

Run No.	Period	Catalyst Base	Catalyst Promoter	Temp °F	Hydrogen Pressure psig	Space Velocity $V_o/hr/V_c$	Space Velocity B/D/Lb	H_2 Rate SCF/Bbl	Catalyst Age Bbl/Lb.	Product Inspections Gravity °API	Product Inspections % S	Product Inspections V ppm	Product Inspections Ni ppm	Product Inspections IBP-550°F,V%
185-192	1B	Porocel 12 x 20 Mesh	---	790	2015	0.83	0.064	3340	0.049	11.0		350	62	Cracked
	2			791	2025	0.83	0.064	3510	0.113	10.5		370	68	Cracked
	3B			791	2000	0.47	0.036	6630	0.158	10.0	2.42	324	67	7.0
	4			788	1995	0.44	0.034	7860	0.186	10.5	2.31	285	62	7.0
	5			790	1995	0.58	0.044	5200	0.230	10.3	2.53	305	66	7.0
	6			790	2000	0.51	0.040	4400	0.270	10.5		284	64	8.0
	7			789	2000	0.51	0.039	4250	0.309	10.6	2.26	262	64	5.0
	8			790	2005	0.54	0.041	4280	0.340	10.4	2.31	261	61	4.0
	9			789	2000	0.55	0.043	3740	0.383	10.2	2.13	265	62	8.0
184-157	1B	Porocel 12 x 20 Mesh	5% Fe	791	1980	0.65	0.049	2580	0.047	10.7	2.42	225	52	5.0
	2			790	2005	0.55	0.042	4130	0.082	11.6	2.20	225	54	6.0
	3			790	2010	0.49	0.037	4570	0.119	11.7	2.32	210	56	8.0
	4			790	2010	0.49	0.037	4440	0.156	13.2	2.19	210	62	8.0
	5			790	2000	0.53	0.041	4100	0.197	12.8	2.16	215	58	7.0
	6			788	1990	0.55	0.042	3350	0.239	11.9	2.28	245	54	6.0
	7			789	2005	0.53	0.040	4290	0.279	11.5	2.11	226	51	8.0
	8			789	2000	0.49	0.037	4150	0.311	10.6	2.18	238	55	10.0
185-193	1B	Porocel 12 x 20 Mesh	5% Co	790	2015	0.62	0.046	3650	0.051	10.5	2.40	276	61	6.0
	2			790	2000	0.55	0.041	4100	0.087	10.3	2.21	266	63	7.0
	3			790	2000	0.55	0.042	3640	0.129	10.7	2.30	252	63	8.0
	4			790	1985	0.46	0.035	4140	0.160	12.6	2.35	235	57	7.0
185-194	1B	Porocel 12 x 20 Mesh	5% Mo	790	2025	0.61	0.045	4140	0.037	14.9	1.24	235	40	7.0
	2			791	2010	0.50	0.038	3870	0.075	15.1	1.04	175	39	7.0
	3			790	2000	0.53	0.040	3630	0.110	14.6	1.27	203	43	7.0
184-158	1B	Porocel 12 x 20 Mesh	5% V	788	2000	0.53	0.040	4090	0.045	12.5	2.30	194	48	7.0
	2			789	1980	0.56	0.042	3830	0.087	12.1	2.20	240	53	5.0
	3			790	1995	0.55	0.041	3770	0.128	12.5	2.34	222	64	7.0
	4			790	2010	0.52	0.039	2700	0.167	12.9	2.32	210	55	6.0

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Table C-1 (continued). SUMMARY OF CATALYST SCREENING RUNS

(Feed: Tia Juana Vacuum Bottoms)

Run No.	Period	Catalyst Base	Catalyst Promoter	Temp °F	Hydrogen Pressure psig	Space Velocity $V_o/hr/V_c$	Space Velocity B/D/Lb	H_2 Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections Gravity °API	Product Inspections % S	Product Inspections V ppm	Product Inspections Ni ppm	Product Inspections IBP-550°F, V%
184-166	1B	Porocel	2% Mo	791	2000	0.58	0.046	4060	0.037	14.7	1.49	142	44	10.0
	2	20 x 50 Mesh		790	2000	0.56	0.044	3820	0.081	16.1	1.02	125	46	12.0
	3			790	2010	0.53	0.042	4370	0.123	16.1	1.00	128	43	8.0
	4			790	2005	0.55	0.043	3770	0.166	16.4	1.19	135	47	8.0
	5			790	2010	0.52	0.041	4030	0.207	15.2	1.13	137	46	8.0
	6			790	2040	0.50	0.039	3940	0.246	15.3	1.08	134	45	8.0
	7			790	1995	0.49	0.038	3620	0.279	15.4	1.06	133	45	5.0
185-209	1B	Porocel	0.5% Mo	790	2000	0.54	0.044	4250	0.041	15.5	1.70	195	46	5.0
	2	12 x 20 Mesh		790	2000	0.49	0.040	4570	0.081	13.8	1.77	196	48	8.0
	3			790	2030	0.63	0.051	3160	0.132	14.4	1.84	207	53	6.0
	4			789	1905	0.54	0.044	3740	0.176	14.0	1.63	192	52	5.0
	5			790	2000	0.54	0.044	3870	0.214	13.5	1.62	188	55	8.0
185-207	1B	Porocel	2% Mo	787	1010	0.88	0.068	3460	0.052	11.7	2.00	260	64	5.0
	2	20 x 50 Mesh		791	1000	0.54	0.042	4320	0.094	14.4	1.59	237	55	9.0
	3			791	1000	0.50	0.038	4260	0.127	13.9	1.67	236	56	10.0
184-167	1B	Porocel		790	2000	0.58	0.042	4200	0.039	14.1	2.32	272	69	6.0
	2	20 x 50 Mesh		790	2010	0.51	0.037	4350	0.076	14.2	2.56	228	63	8.0
	3			790	2000	0.43	0.031	4920	0.103	13.1	1.86	208	64	9.0
184-168	1B	Porocel	1% Zn	791	2005	0.55	0.044	4410	0.037	12.4	2.43	252	60	6.0
	2			792	1995	0.47	0.038	3670	0.075	12.5	2.23	234	63	12.0
	3			791	1995	0.52	0.042	3850	0.117	13.7	2.23	261	64	10.0
185-208	1B	Attapulgus		790	2010	0.51	0.073	3880	0.089	13.8	2.12	157	47	9.0
	2	Activated		789	1990	0.44	0.062	5510	0.151	14.1	2.24	170	51	11.0
	3	Clay		790	1995	0.53	0.075	4190	0.226	13.5	2.23	194	57	10.0
	4	30 x 60 Mesh		789	1975	0.50	0.071	5770	0.297	14.5	2.19	208	52	8.0
	5			791	1995	0.52	0.074	4500	0.371	12.3	2.10	220	57	9.0
	6			789	2000	0.54	0.076	4560	0.447	11.4	2.32	297	63	7.0

Table C-1 (continued). SUMMARY OF CATALYST SCREENING RUNS

(Feed: Tia Juana Vacuum Bottoms)

						Space Velocity				Product Inspections				
Run No.	Period	Catalyst Base	Catalyst Promoter	Temp °F	Hydrogen Pressure psig	$V_o/hr/V_c$	B/D/Lb	H_2 Rate SCF/Bbl	Catalyst Age Bbl/Lb.	Gravity °API	% S	V ppm	Ni ppm	IBP-550°F,V%
184-165	1B	Porocel	2% Mo	790	2000	0.46	0.036	4300	0.033	14.6	1.76	241	48	2.0
	2	12 x 20 Mesh		790	2010	0.48	0.037	4550	0.070	15.9	1.35	176	40	3.0
	3			790	1985	0.51	0.040	3900	0.110	15.4	1.11	185	50	7.0
	4			790	2000	0.53	0.042	3800	0.152	15.2	1.41	191	50	11.0
	5			790	2010	0.52	0.041	3990	0.193	15.9	1.23	193	46	8.0
	6			791	2000	0.52	0.041	4000	0.234	14.4	1.26	210	50	11.0
	7			790	2005	0.53	0.041	4130	0.275	15.9	1.32	211	50	8.0
	8B			791	2020	0.33	0.026	5780	0.308	15.8	1.10	170	45	8.0
	9			789	2000	0.38	0.030	4980	0.338	15.9	1.10	162	44	8.0
	10B			789	2005	0.49	0.038	4980	0.377	15.5	1.22	217	50	8.0
	11			790	2000	0.53	0.041	4230	0.413	14.4	1.28	217	49	11.0
185-203	1B	ACCO Porous	8.9% Mo	789	2000	0.49	0.058	4820	0.068	16.9	1.41	204	42	7.0
	2	Al_2O_3		789	1985	0.54	0.065	4000	0.133	15.8	1.43	240	44	10.0
	3	(1/16")		790	2000	0.53	0.064	4400	0.189	14.5	1.56	248	45	9.0
185-204	1B	Attapulgus	2% Mo	790	1995	0.60	0.083	3980	0.084	14.7	2.03	208	45	5.0
	2	Activated		794	2000	0.52	0.072	4050	0.156	14.4	1.97	205	46	7.0
	3	Clay		790	2000	0.47	0.065	4630	0.221	15.1	2.09	214	53	5.0
	4			790	2005	0.59	0.082	3420	0.303	13.1	2.10	263	59	9.0
	5			790	1995	0.43	0.060	4880	0.363	13.8	2.36	325	58	7.0
	6			790	2005	0.57	0.079	3740	0.432	13.3	2.07	264	58	9.0
185-205	1B	Porocel	1% Mo	788	2000	0.54	0.045	4890	0.037	14.5	1.73	178	45	7.0
	2	12 x 20 Mesh		790	1995	0.51	0.043	4600	0.080	14.2	1.41	168	49	7.0
	3			790	1980	0.53	0.044	4230	0.124	13.9	1.48	186	50	7.0
	4			790	2000	0.54	0.045	3810	0.169	13.5	1.41	193	52	7.0
	5			790	2000	0.52	0.044	3740	0.213	14.9		191	51	7.0
	6			791	2000	0.48	0.040	4720	0.253	14.6	1.41	178	51	7.0
	7			789	2000	0.53	0.044	4440	0.292	14.8	1.36	193	53	8.0

Table C-1 (continued). SUMMARY OF CATALYST SCREENING RUNS

(Feed: Tia Juana Vacuum Bottoms)

Run No.	Period	Catalyst Base	Catalyst Promoter	Temp °F	Hydrogen Pressure psig	Space Velocity		H_2 Rate SCF/Bbl	Catalyst Age Bbl/Lb.	Product Inspections				
						$V_o/hr/V_c$	B/D/Lb			Gravity °API	% S	V ppm	Ni ppm	IBP-550°F,V%
185-195	1B	Porocel 12 x 20 Mesh	H_3PO_4	789	1970	0.56	0.044	2880	0.049	12.6	2.54	308	64	5.0
	2			790	1995	0.53	0.041	3990	0.090	11.4	2.62	310	68	6.0
	3			790	2005	0.57	0.044	3200	0.134	11.3	2.54	280	65	6.0
184-159	1B	Porocel 12 x 20 Mesh	7/ Ni	787	1990	0.49	0.037	4290	0.033	13.6	2.33	217	57	7.0
	2			790	1990	0.50	0.038	4020	0.065	13.3	2.31	220	62	6.0
	3			797	1995	0.56	0.043	3950	0.103	14.2	2.27	240	62	8.0
185-196	1B	Porocel 12 x 20 Mesh	5/ C_R	788	1950	0.59	0.044	2710	0.031	11.9	2.50	223	57	6.0
	2			790	1995	0.57	0.042	3808	0.071	11.7	2.53	253	58	8.0
	3			790	2005	0.49	0.036	3537	0.102	14.7	2.30	247	55	9.0
184-160	1B	Porocel 12 x 20 Mesh	10/ Fe	790	2000	0.56	0.043	3480	0.042	13.8	2.32	215	45	6.0
	2			791	1985	0.54	0.042	3220	0.084	12.1	2.24	222	49	8.0
	3			789	2005	0.54	0.042	4000	0.126	12.1	2.40	217	49	8.0
	4			790	2000	0.55	0.042	3580	0.163	12.9	2.36	230	51	6.0
185-197	1B	Porocel 12 x 20 Mesh	10/ V	789	2000	0.63	0.046	3260	0.035	12.9	2.31	198	45	4.0
	2			791	2000	0.60	0.041	3530	0.076	12.3	2.18	190	50	5.0
	3			789	1990	0.50	0.036	3660	0.107	14.1	2.04	202	53	5.0
185-198	------------ Run terminated on startup due to charge pump failure ------------													
184-161	1B	Low SiO_2 Porocel (Silica)	5/ Fe	790	2005	0.59	0.046	3840	0.043	13.0	2.45	260	60	6.0
	2			790	2005	0.53	0.041	4190	0.084	13.3	2.18	250	58	9.0
	3			790	2000	0.49	0.039	3890	0.118	13.2	2.32	224	55	8.0
184-162	1B	Porocel 12 x 20 Mesh	1.5/ Co/ 5/ Mo	795	2000	0.71	0.054	3480	0.050	16.2	1.05	194	42	6.0
	2			790	2010	0.54	0.041	4050	0.091	15.5	1.14	186	42	7.0
	3			790	2000	0.57	0.043	3970	0.134	15.1	1.14	200	47	6.0
	4			786	2000	0.47	0.036	4380	0.170	15.1	1.31	196	46	8.0
	5			790	1990	0.54	0.041	3920	0.211	15.4	1.24	203	46	7.0
	6			790	1985	0.53	0.040	3860	0.246	14.1	1.21	205	45	8.0

Table C-1 (continued). SUMMARY OF CATALYST SCREENING RUNS

(Feed: Tia Juana Vacuum Bottoms)

Run No.	Period	Catalyst Base	Catalyst Promoter	Temp °F	Hydrogen Pressure psig	Space Velocity		H_2 Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
						V_o/hr/V_c	B/D/Lb			Gravity °API	% S	ppm	ppm	IBP-550°F, V%
185-199	1B	Activated Clay (Engelhard)	----	792	2000	0.47	0.069	6380	0.083	13.2	2.23	234	48	6.0
	2			791	2005	0.56	0.082	3860	0.165	12.4	2.11	236	54	7.0
	3			791	2000	0.50	0.074	4200	0.239	13.5	2.09	255	57	8.0
	4			790	2010	0.53	0.077	3110	0.316	12.7	2.31	274	59	7.0
	5			790	2000	0.48	0.070	3930	0.386	12.9	2.17	266	62	8.0
	6			790	1990	0.58	0.085	3760	0.471	12.7	2.12	289	59	7.0
	7			789	2000	0.52	0.077	3500	0.516	13.2	2.25	243	59	6.0
184-163	1B	Al_2O_3 (35 M^2/g-HRI 1243 - 12 x 20 Mesh)	5% Mo	792	2010	0.58	0.053	3980	0.046	14.6	1.83	176	52	6.0
	2			790	2000	0.53	0.049	4040	0.084	14.3	2.10	176	56	8.0
	3			790	2000	0.51	0.047	2660	0.130	13.1	2.07	207	58	8.0
	4			790	2010	0.55	0.050	5060	0.174	14.0	2.05	215	59	10.0
	5			787	2005	0.49	0.045	4140	0.219	13.5	2.10	204	61	9.0
	6			790	2005	0.53	0.048	3720	0.228	12.5	1.99	232	67	8.0
185-200	1B	Activated Clay	9.5% Mo	790	1995	0.49	0.060	4180	0.059	14.1	1.88	170	42	7.0
	2			790	1990	0.48	0.058	4390	0.117	14.6	1.80	197	46	8.0
	3			789	2005	0.57	0.070	3420	0.187	15.2	2.11	246	53	7.0
	4			787	2010	0.43	0.052	4690	0.233	14.0	1.96	207	60	8.0
184-164	1B	Al_2O_3 (HRI 1243) Macroporous 12 x 20 Mesh)	5% Fe	790	2020	0.58	0.051	3870	0.047	13.2	2.47	300	69	5.0
	2			788	2020	0.55	0.048	3960	0.095	12.5	2.36	274	67	6.0
185-201	1B	CAL (Activated Carbon)	11% Mo	791	1995	0.48	0.075	4070	0.059	16.2	1.57	224	47	7.0
	2			790	2010	0.54	0.085	3670	0.144	14.9	1.81	249	53	6.0
	3			790	2005	0.61	0.096	3610	0.212	14.2	1.77	272	52	6.0
185-202	1B	Low Surface Area Al_2O_3 (HRI 3443)	3.8% Mo	790	2000	0.56	0.029	3570	0.029	12.9	2.59	448	75	3.0
	2			790	1995	0.45	0.023	4430	0.052	9.3	2.59	413	72	5.0

Table C-1 (continued). SUMMARY OF CATALYST SCREENING RUNS

Run No.	Period	Catalyst Base	Catalyst Promoter	Temp °F	Hydrogen Pressure psig	Space Velocity		H₂ Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
						V_o/hr/V_c	B/D/Lb			Gravity °API	% S	V ppm	Ni ppm	IBP-550°F,V%
184-169	1B	Porocel 20 × 50 Mesh	0.5% Mo	790	2000	0.49	0.038	4400	0.039	14.5	1.71	162	45	7.0
	2			790	2000	0.51	0.040	3910	0.079	12.9	1.62	145	48	11.0
	3			790	2005	0.52	0.041	3940	0.120	14.9	1.55	153	49	8.0
	4			790	2010	0.50	0.038	3820	0.158	15.2	1.62	140	48	9.0
	5			791	2010	0.58	0.045	3720	0.203	13.6	1.54	155	49	8.0
	6			789	2000	0.50	0.038	4020	0.236	15.2	1.62	149	48	8.0
184-171	1B	Porocel 20 × 50 Mesh	1% Mn	792	2000	0.49	0.038	4020	0.032	14.4	2.22	190	48	8.0
	2			789	2000	0.50	0.038	4210	0.070	14.6	2.12	199	52	9.0
	3			790	2000	0.53	0.041	3090	0.106	13.7	2.22	181	59	8.0

APPENDIX D

SUMMARY OF DEMETALLIZATION RUNS

Table D-1. SUMMARY OF DEMETALLIZATION RUNS

						Space Velocity				Product Inspections				
Run No.-Period	Catalyst Base	Catalyst Promoter	Feed	Temp °F	H_2 Pres. psig	$V_o/hr/V_c$	B/D/Lb	H_2 Rate SCF/Bbl	Cat. Age Bbl/Lb	Gravity °API	% S	V ppm	Ni ppm	IBP-550°F V%
185-210-8B	Porocel	2/ Mo	Tia Juana	791	2005	0.64	0.048	2670	0.308	14.6	1.36	191	54	6.0
9	(184-166 Dump		V.B.	790	2005	0.63	0.048	3820	0.356	15.4	1.25	179	51	8.0
10	20 x 50 Mesh)			791	2010	0.56	0.043	4480	0.399	16.2	1.25	172	51	6.0
11				789	2010	0.56	0.043	4480	0.442	15.7	1.35	176	47	7.0
12				791	1995	0.48	0.037	4370	0.479	15.0	1.31	220	54	7.0
13				789	2015	0.38	0.029	5400	0.508	15.9	1.25	170	44	9.0
14				788	1990	0.47	0.036	4510	0.544	15.9	1.27	183	49	7.0
15				787	2010	0.42	0.032	7830	0.549	14.6	1.36	185	47	6.0
184-172-21B	Porocel		Gach Saran	791	2000	0.69	0.054	4230	0.055	13.1	2.24	115	78	6.0
22	(201-58 Dump)		V.B.	790	2010	0.78	0.060	3990	0.115	13.4	2.17	98	75	7.0
23				708	1985	0.74	0.057	4060	0.165	12.9	2.16	92	74	7.0
185-211-1B	Porocel	2/ Mo	Tia Juana	790	2015	0.43	0.032	4690	0.031			97	29	
2	(20 x 50 Mesh)		V.B.	789	2005	0.43	0.032	5130	0.063	16.3	1.09	92	32	8.0
3				790	2005	0.46	0.035	4290	0.098	16.3	1.10	106	38	8.0
4				792	2010	0.48	0.036	4960	0.134	16.4	1.15	120	42	10.0
5				790	2015	0.50	0.038	4550	0.172	16.1	1.22	134	46	9.0
6				789	2005	0.50	0.038	4820	0.211	15.5	1.20	149	49	10.0
7				790	2000	0.46	0.035	4460	0.246	15.8	0.97	145	43	10.0
8				792	2005	0.47	0.035	4240	0.281	15.5	1.33	155	45	9.0
9				792	2000	0.48	0.036	5120	0.317	15.9	1.24	163	48	10.0
10				790	2000	0.51	0.038	4070	0.355	15.4	1.51	212	54	8.0
11				793	2000	0.49	0.037	4950	0.392	15.8	1.45	194	52	9.0
12				791	2005	0.47	0.035	4400	0.425	15.7	1.32	191	53	8.0
13				789	1995	0.51	0.039	4460	0.464	15.8	1.34	195	51	8.0
14				791	2005	0.49	0.037	5820	0.501	14.8	1.50	254	57	13.0
15				790	2000	0.47	0.035	3910	0.532	15.0	1.60	212	52	8.0
185-212-1B	HDS-1442B		Tia Juana	790	1980	0.52	0.071	4000	0.061	17.8	0.69	50	22	4.0
2	(HRI 3456)		V.B.	790	1995	0.51	0.068	4270	0.129	17.4	0.74	105	34	10.0
3	Crushed to			790	1990	0.49	0.066	4310	0.195	16.6	0.90	89	33	8.0
4	20 x 50 Mesh			790	2000	0.59	0.080	4330	0.275	16.5	0.92	123	36	7.0
5				788	2005	0.52	0.071	4060	0.364	16.8	0.89	101	37	7.0

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Table D-1 (continued). SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst Base	Catalyst Promoter	Feed	Temp °F	H_2 Pres. psig	Space Velocity		H_2 Rate SCF/Bbl	Cat. Age Bbl/Lb	Product Inspections				
						$V_o/hr/V_c$	B/D/Lb			Gravity °API	% S	V ppm	Ni ppm	IBP-550°F V %
185-213-1B	Porocel	2/ Mo	Bachaquero	789	2000	1.00	0.075	4110	0.058	14.9	1.75	176	53	6.0
2	(20 × 50 Mesh)		V.B.	790	2010	1.00	0.075	3900	0.133	14.9	1.49	193	59	6.0
3				790	2005	1.04	0.078	4160	0.211	14.4	1.61	209	64	6.0
4				790	2000	0.73	0.054	3900	0.265	15.2	1.52	168	61	8.0
5				790	2020	0.73	0.055	4250	0.320	14.9	1.17	174	62	10.0
6				790	2000	0.71	0.053	4110	0.373	15.1	1.22	171	61	9.0
7				789	1995	0.77	0.058	5470	0.431	14.8	1.36	188	62	8.0
8				790	1985	0.73	0.054	4380	0.485	15.2	1.50	183	60	8.0
9				789	2010	0.75	0.056	4400	0.541	14.7	1.62	186	60	8.0
10				791	2000	0.73	0.055	4310	0.596	14.3	1.44	189	67	9.0
11				787	1990	0.53	0.039	4100	0.635	14.1		157	50	
12				791	2000	0.59	0.044	3790	0.679	12.8		330	74	
13				790	2005	0.64	0.047	4750	0.726	14.2	2.45	455	99	9.0
14				789	2000	0.69	0.051	6010	0.745	14.0				
185-214-1B	Porocel	2/ Mo	Bachaquero	791	1995	0.93	0.069	4130	0.064	18.1	1.59	167	54	7.0
2	(20 × 50 Mesh)		V.B.	790	1990	0.95	0.070	2600	0.134	13.5	1.82	267	73	8.0
3				790	2005	1.01	0.075	4220	0.209	13.8	1.71	342	83	8.0
4				791	1990	0.73	0.054	4810	0.263	14.2	1.52	243	70	7.0
5				792	2000	0.75	0.056	3330	0.319	13.2	1.64	312	77	8.0
6				790	2000	0.70	0.052	4140	0.371	14.0	1.52	270	65	7.0
184-174-1B	Porocel	2/ Mo	Tía Juana	792	2000	0.92	0.067	4090	0.089	16.4	1.23	151	47	7.0
2	(20 × 50 Mesh)		V.B.	790	2005	0.99	0.072	4000	0.161	15.0	1.31	175	48	6.0
3				792	2000	0.97	0.070	4160	0.231	15.2	1.52	179	60	5.0
4				792	1990	0.72	0.052	4150	0.283	14.9	1.30	159	52	9.0
5				791	1990	0.77	0.056	4010	0.339	15.0	1.39	169	54	8.0
6				791	1995	0.74	0.054	4050	0.393	15.2	1.20	174	52	8.0
7				790	2005	0.72	0.052	4320	0.445	15.3	1.45	174	44	6.0
8				791	2000	0.72	0.052	3990	0.497	15.0	1.39	174	45	6.0
9				790	2000	0.71	0.051	4130	0.548	15.7	1.31	168	42	6.0
10				790	2000	0.74	0.054	4220	0.602	15.5	1.34	172	45	6.0
11				790	2010	0.76	0.055	4060	0.678	14.3	1.61	192	53	5.0
12				792	2005	0.75	0.055	3940	0.753	13.7	1.37	185	48	3.0
13				791	2015	0.76	0.055	3940	0.808	14.8	1.33	183	56	7.0

Table D-1 (continued). SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst Base	Catalyst Promoter	Feed	Temp. °F	H_2 Pres. psig	Space Velocity		H_2 Rate SCF/Bbl	Cat. Age Bbl/Lb	Product Inspections				
						$V_o/hr/V_c$	B/D/Lb			Gravity °API	% S	V ppm	Ni ppm	IBP-550°F V %
184-174-14	Porocel (20 × 50 Mesh)	2% Mo	Tia Juana V.B.	791	2000	0.71	0.052	4400	0.879	14.2	1.34	173	58	4.0
15				792	1995	0.75	0.054	4330	0.933	14.9	1.33	193	49	7.0
16				791	1995	0.72	0.052	4400	0.985	14.9	1.58	198	55	7.0
17				790	1990	0.73	0.053	4080	1.038	14.3	1.53	217	51	3.0
18				790	1990	0.72	0.052	4220	1.090	14.1	1.50	218	51	9.0
19				789	1985	0.76	0.055	3880	1.145	13.5	1.56	226	52	8.0
20				788	1980	0.78	0.057	3780	1.202	14.1	1.51	226	54	8.0
21B				791	1990	0.36	0.026	5500	1.239	15.9	1.23	149	37	9.0
22				792	1995	0.51	0.037	4270	1.271	15.0	1.19	178	44	9.0
185-215-1B	Porocel (20 × 50 Mesh)	2% Mo	Bachaquero V.B.	790	2000	1.01	0.075	3270	0.064	16.7	1.53	174	57	6.0
2				789	1995	0.98	0.072	3910	0.136	14.5	1.42	190	63	7.0
3				790	1995	0.96	0.071	3650	0.207	14.0	1.63	208	64	7.0
4				791	1990	0.78	0.058	3820	0.265	13.8	1.95	183	60	8.0
5				789	2000	0.70	0.052	4270	0.317	13.7	1.59	225	63	9.0
6				790	2010	0.73	0.054	4790	0.371	13.3	1.93	341	80	9.0
7				792	2005	0.77	0.057	3790	0.428	13.5	1.89	282	70	12.0
8				790	2000	0.67	0.050	5120	0.478	13.5	1.89	282	70	12.0
9				788	2000	0.76	0.056	4190	0.534	14.5	1.80	283	71	9.0
185-216-1B	Porocel (20 × 50 Mesh)	2/ Mo	Bachaquero V.B.	791	1990	0.95	0.074	4650	0.064	16.1	1.62	189	61	8.0
2				791	2000	0.94	0.073	5000	0.137	14.4	1.44	183	60	8.0
3				790	2000	0.95	0.074	3990	0.211	14.3	1.42	202	71	6.0
4				787	2000	0.69	0.054	5840	0.265	13.9	1.49	172	75	9.0
5				789	2030	0.78	0.0060	4910	0.325	12.9	1.42	179	56	6.0
6				791	2020	0.68	0.053	5960	0.378	15.2	1.18	158	52	10.0
7				789	1990	0.75	0.059	4560	0.437	14.3	1.48	197	56	9.0
185-217-1B	Regular Porocel		Bachaquero V.B.	790	2000	0.61	0.049	4720	0.046	11.5	2.76	311	76	9.0
2				792	2010	0.65	0.052	6590	0.081	11.9	2.89	340	84	12.0

Table D-1 (continued). SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst Base	Catalyst Promoter	Feed	Temp °F	H2 Pres. psig	Space Velocity $V_o/hr/V_c$	Space Velocity B/D/Lb	H2 Rate SCF/Bbl	Cat. Age Bbl/Lb	Product Inspections Gravity °API	Product Inspections % S	Product Inspections V ppm	Product Inspections Ni ppm	Product Inspections IBP-550°F V%
201-68	Attrited 185-211 Dump, 75% Initial Chg.			-------------- Charge pump failure. Run terminated during startup ------------------										
184-173-1B	Porocel 20 x 50 Mesh	2% Mo	Gach Saran V.B.	791	2000	0.74	0.056	4040	0.044	15.9	1.01	31	19	6.0
2				790	2000	0.70	0.052	4310	0.096	15.3	0.91	33	31	7.0
3				790	2000	0.70	0.052	4230	0.149	15.1	0.98	41	37	7.0
4				790	2020	0.73	0.055	4090	0.204	16.7	1.08	41	42	8.0
5				788	1995	0.75	0.056	3810	0.260	14.9	1.39	47	45	10.0
6				790	2000	0.76	0.057	4030	0.317	14.4	1.13	49	45	8.0
7				791	2020	0.76	0.057	4090	0.374	15.7	1.26	50	45	7.0
8				790	2005	0.75	0.056	3910	0.430	14.7	1.10	47	48	7.0
9				791	1995	0.98	0.073	3670	0.503	13.9	1.46	61	58	7.0
10				790	2000	0.99	0.074	3650	0.577	14.0	1.40	63	57	7.0
11				790	2000	1.00	0.075	3640	0.652	14.3	1.43	62	55	7.0
12				790	2005	1.00	0.075	3820	0.727	14.4	1.20	64	57	7.0
13				790	2000	0.98	0.073	4100	0.797	14.0	1.35	64	57	7.0
14				790	2000	1.01	0.675	4070	0.872	13.8	1.14	70	59	7.0
15				789	2000	0.98	0.073	4190	0.945	14.5	1.35	63	56	7.0
16				790	2000	0.97	0.072	4230	1.017	14.7	1.58	60	59	7.0
17				790	1995	0.93	0.070	4160	1.087	14.1	1.44	58	56	7.0
18				790	1995	0.94	0.071	4260	1.198	13.9	1.49	65	54	7.0
19				790	1995	1.02	0.076	4000	1.234	13.8	1.14	68	56	6.0
20				791	2000	1.01	0.075	3990	1.309	14.1	1.61	74	57	6.0
21				790	2005	1.01	0.076	3930	1.385	14.0	1.45	74	57	7.0
22				790	2000	0.98	0.073	4060	1.458	13.9	1.64	80	55	7.0
23				791	2000	0.98	0.073	4040	1.531	13.8	1.70	87	56	7.0
24				791	2000	0.96	0.072	4210	1.603	14.4	1.64	88	64	8.0
25				790	1980	0.96	0.072	4220	1.675	14.4	1.62	100	63	7.0
26				792	1965	0.71	0.053	4200	1.728	14.2	1.42	91	54	11.0
27				791	2020	0.72	0.054	4030	1.782	14.6	1.43	88	54	10.0
28				790	2010	0.71	0.053	4240	1.828	14.2	1.59	81	54	8.0

APPENDIX E

SUMMARY OF DESULFURIZATION RUNS

Table E-1. SUMMARY OF DESULFURIZATION RUNS

Run No.	Period	Catalyst Base	Feed	Temp. °F	H_2 Pres. psig	Space Velocity $V_o/hr/V_c$	Space Velocity B/D/Lb	H_2 Rate SCF/Bbl	Cat. Age Bbl/Lb	Product Inspections: Gravity °API	Product Inspections: % S	Product Inspections: V ppm	Product Inspections: Ni ppm	Product Inspections: IBP-600°F V/
185-209	1B	American Cyanamid HDS-1442B (HRI 3456) 1/32"	Tia Juana V.B.	790	2020	0.53	0.077	3460	0.063	16.5	1.11	175	41	7.0[a]
	2			791	2010	0.54	0.077	4210	0.134	16.2	0.99	186	42	9.0
	3			791	2000	0.53	0.077	4230	0.211	15.4	1.14	194	48	8.0
	4			790	2015	0.65	0.094	3240	0.305	13.5	1.41	222	52	7.0
	5			790	2000	0.51	0.074	3840	0.379	15.2	1.29	198	44	7.0
	6			791	2010	0.44	0.063	5030	0.434	15.1	1.26	175	52	7.0
201-69	1B	American Cyanamid 0.02" Beads (HRI 3104) 20 x 50 Mesh	Demetallized Gach Saran V.B.	760	2000	1.00	0.105	5680	0.098	17.1	0.57	60	25	9.0
	2			759	1975	1.03	0.108	8820	0.206	16.8	0.39	63	30	8.0
	3			760	1970	1.08	0.112	9290	0.318	15.8	0.41	42	33	9.0
	4			762	1975	1.07	0.111	9690	0.429	16.1	0.36	41	36	8.0
	5			760	1985	1.00	0.105	7230	0.534	16.1	0.28	48	40	9.0
	6			760	1990	0.97	0.102	7040	0.636	16.6	0.51	40	31	6.0
	7			760	1995	0.99	0.104	7650	0.740	16.1	0.39	34	40	7.0
	8			760	1980	1.08	0.112	9080	0.852	16.4	0.37	36	43	5.0
	9			761	1955	1.14	0.120	6500	0.972	16.0	0.37	33	43	5.0
	10			761	1990	1.04	0.109	5380	1.081	16.2				
	11			760	1995	1.04	0.109	7060	1.190	16.4				
	12			760	1985	1.04	0.109	10030	1.299	16.6	0.44	46	39	5.0
	13			761	1990	1.09	0.113	7720	1.412	15.8				
	14			761	1990	0.96	0.101	9820	1.513	16.1	0.56	46	36	6.0
	15			760	1995	1.02	0.107	5970	1.620					
	16			757	1980	1.02	0.107	8680	1.727	16.4	0.41	60	32	<3.0
	17			760	1975	0.95	0.100	8430	1.827	16.0				
	18			761	1995	1.12	0.117	6940	1.944	15.6				
	19			759	1985	1.17	0.122	8100	2.066	15.9	0.54	51	37	4.0
	20			760	1990	1.09	0.113	8650	2.179	15.3				
	21			760	1990	1.08	0.112	7450	2.291	15.7	0.49	43	35	5.0
	22			761	1985	1.13	0.118	12350	2.409	15.8				
	23			759	1985	1.07	0.111	9150	2.520	15.7	0.46	45	36	7.0
	24			760	1980	1.02	0.107	9720	2.627	15.8	0.45			4.0
185-218	1B	American Cyanamid 0.02" Beads (HRI 3104) 20 x 50 Mesh	Demetallized Gach Saran V.B.	762	2000	1.14	0.122	3470	0.098	17.9	0.63	53	26	12.0
	2			760	2005	1.05	0.112	3880	0.210	17.7	0.43	42	27	9.0
	3			758	2010	1.12	0.120	3750	0.333	17.1	0.52	42	30	9.0
	4			761	2000	1.04	0.111	4140	0.441	17.7	0.46	40	29	7.0

a. IBP-550°F for Run 185-209.

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Table E-1 (continued). SUMMARY OF DESULFURIZATION RUNS

										Product Inspections				
Run No.	Period	Catalyst Base	Feed	Temp °F	H_2 Pres. psig	Space Velocity $V_o/hr/V_c$	Space Velocity B/D/Lb	H_2 Rate SCF/Bbl	Cat. Age Bbl/Lb	Gravity °API	% S	V ppm	Ni ppm	IBP-600°F V%
185-219	1B	American Cyanamid 0.02"	Demetallized	762	1990	0.76	0.081	5920	0.087	16.8	0.97	167	41	8.0
	2	Beads (HRI 3104)	Tia Juana	759	2000	0.73	0.078	6820	0.165	17.4	0.43	161	39	9.0
	3	20 x 50 Mesh	V.B.	759	1990	0.72	0.077	8150	0.242	17.1	0.64	188	37	8.0
	4			760	2000	0.74	0.079	5850	0.321	17.2	0.48	179	34	8.0
184-175	1B	American Cyanamid 0.02"	Demetallized	755	2000	1.05	0.112	3910	0.101	17.1	0.66	144	36	7.0[b]
	2	Beads (HRI 3104)	Tia Juana	759	2010	1.19	0.127	3790	0.228	16.6	0.47	137	40	5.0
	3	20 x 50 Mesh	V.B.	759	2050	1.03	0.110	5020	0.338	16.7	0.57	147	43	3.0
	4			760	2000	1.07	0.114	4270	0.452	16.2	0.51	141	39	3.0
	5			758	2000	1.04	0.111	4330	0.563	16.1	0.62	146	41	2.0
	6			760	1995	1.03	0.110	3860	0.673	16.6	0.62	147	44	3.0
	7			760	1995	0.99	0.106	4340	0.779	16.4	0.48	151	54	<1.0
	8			761	2000	1.05	0.112	3920	0.891	16.3	0.73	149	51	2.0
	9			761	2030	1.03	0.109	4040	1.000	15.3				
	10			760	2025	1.21	0.130	3780	1.130	15.5				
	11			760	2000	1.15	0.123	3400	1.253	15.6	0.57	149	50	4.0
	12			760	2000	1.07	0.114	4320	1.367	16.2				
	13			759	2005	1.04	0.111	4570	1.478	16.7	0.62	140	45	5.0
	14			762	2005	1.04	0.111	5690	1.589	16.1				
	15			760	1990	0.87	0.093	6540	1.682	17.2	0.60	156	39	5.0
	16			762	2000	0.87	0.093	4880	1.775	16.6				
	17			761	2000	0.87	0.093	4970	1.868	16.5				
	18			759	2000	0.90	0.096	4910	1.964	16.6	0.52	159	40	3.0
	19			760	1985	0.95	0.101	4820	2.065	17.0				
	20			761	1990	1.02	0.109	4580	2.174	16.4	0.65	157	44	4.0
	21			759	1995	1.01	0.108	4550	2.282	16.4				
	22			759	2000	0.97	0.103	5000	2.385	16.0	0.70	160	43	4.0
	23			760	1990	1.00	0.107	4560	2.492	15.9				
	24			761	2000	0.94	0.100	4060	2.592	16.2				
	25			760	2000	0.94	0.100	4030	2.692	16.1	0.65	155	42	4.0
	26			759	1995	0.93	0.099	4380	2.791	16.3				
	27			759	1995	0.94	0.100	4300	2.891	15.5	0.67	154	40	5.0
	28			760	1990	0.92	0.098	4700	2.989	15.9				
	29			760	1990	0.92	0.098	4530	3.087	17.2	0.51	150	39	5.0

b. IBP-550°F for Run 184-175

Table E-1 (continued). SUMMARY OF DESULFURIZATION RUNS

Run No.	Period	Catalyst Base	Feed	Temp °F	H_2 Pres. psig	Space Velocity $V_o/hr/V_c$	Space Velocity B/D/Lb	H_2 Rate SCF/Bbl	Age Bbl/Lb	Product Inspections Gravity °API	Product Inspections % S	Product Inspections V ppm	Product Inspections Ni ppm	Product Inspections IBP-600°F V%
201-70	1B	American Cyanamid 0.02" Beads (HRI 3104) 12 x 50 Mesh	Demetallized Bachaquero V.B.	760	2020	1.04	0.111	5030	0.096	17.0	0.56	109	40	13.0
	2			760	2040	0.92	0.098	5740	0.188	17.6	0.57	120	47	11.0
	3			761	2015	1.20	0.127	5670	0.315	16.4	0.59	136	43	12.0
	4			760	1980	1.23	0.131	4050	0.446	15.5	0.62	145	44	11.0
	5			762	2015	1.11	0.118	3720	0.564	15.7	0.56	145	45	9.0
	6			761	2025	1.15	0.122	3250	0.686	15.3	0.55	141	46	7.0
	7			760	2010	1.10	0.117	3930	0.803	15.7	0.66	139	46	7.0
	8			759	2015	1.10	0.118	4730	0.921	16.5	0.60	159	49	8.0
	9			758	2015	0.80	0.085	5880	1.006	15.6	0.56	148	45	8.0
	10			759	2000	0.88	0.094	5960	1.100					
	11			761	1985	0.99	0.106	4900	1.206	15.5				
	12			760	2010	0.95	0.101	4170	1.307	16.1	0.60	154	48	4.0
	13			761	1990	0.99	0.106	3495	1.413	15.7				
	14			760	2015	0.98	0.105	4250	1.518	15.6	0.63	164	50	4.0
	15			760	1990	1.04	1.111	4590	1.629	15.4				
	16			760	2000	0.99	0.106	4850	1.735	16.1	0.57	155	46	6.0
	17			760	2030	0.93	0.099	4430	1.834	15.1				
	18			761	2010	1.05	0.112	3790	1.946	15.3				
	19			760	1985	0.94	0.100	6240	2.046	15.5	0.75	154	45	8.0
	20			760	2000	0.88	0.094	5510	2.140	15.4				
	21			760	1990	0.86	0.092	5620	2.232	16.2	0.60	152	48	10.0
	22			762	2050	0.96	0.103	4550	2.335	16.0				
	23			760	1995	0.94	0.100	5340	2.435	15.8	0.63	151	46	7.0
	24			761	2005	0.85	0.091	5180	2.526	14.8				
	25			763	2000	0.87	0.093	4810	2.619	14.9	0.61			8.0
	26			759	2000	0.91	0.097	5140	2.716	15.2	0.66		53	7.0

APPENDIX F

OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

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Table F-1. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	184-166-5
Catalyst Age, Bbl/Lb	0.21
Feed	Tia Juana Vacuum Bottoms
HRI No. (Feed)	2414
Catalyst	LX-22

OPERATING CONDITIONS

Hydrogen Pressure, psig	2010
Temperature, °F	790
Liquid Space Velocity, V/hr/V	0.52
Catalyst Space Velocity, B/D/Lb	0.041
Hydrogen Rate, SCF/B	4030
Reactor Type	Downflow
Hydrogen Consumption, SCF/B	730
975°F+ Conversion, V %	21.0

YIELDS

Cut Points	H_2S & NH_3	C_1-C_3[a]	C_4-C_6[a]	IBP-400°F	400-650°F	650-975°F	975°F+	400°F+	Collected Liquid
W %	2.1	0.7	0.4	2.7	6.6	19.8	68.8	95.2	
V %			0.6	3.6	7.8	21.7	70.3	99.8	103.4
Gravity, °API				50.0	31.7	19.9	9.6	14.2	15.2
Sulfur, W %				<0.02	0.22	0.83	1.47	1.25	1.13
Flash Point, °F								335	
Pour Point, °F								60.0	
Carbon, W %									85.81
Hydrogen, W %									11.52
Nitrogen, ppm									4200
Bromine No.				8.2	10.5				
Vis SFS @ 210°F								60.0	
RCR, W %							19.6		
Vanadium, ppm							194.0		
Nickel, ppm							64.0		

a. Calculated from correlation.

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Table F-2. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	185-211-3
Catalyst Age, Bbl/Lb	0.10
Feed	Tia Juana Vacuum Bottoms
HRI No. (Feed)	2414
Catalyst	LX-22-3

OPERATING CONDITIONS

Hydrogen Pressure, psig	2005
Temperature, °F	790
Liquid Space Velocity, V/hr/V	0.46
Catalyst Space Velocity, B/D/Lb	0.035
Hydrogen Rate, SCF/B	4290
Reactor Type	Downflow
Hydrogen Consumption, SCF/B	615
975°F+ Conversion, V %	24

YIELDS

Cut Points	H_2S & NH_3	C_1-C_3[a]	C_4-C_6[a]	IBP-400°F	400-650°F	650-975°F	975°F	400°F+	Collected Liquid
W %	2.2	0.8	0.4	2.7	7.7	21.2	65.9	94.8	
V %			0.7	3.7	9.3	23.3	67.4	100.0	103.7
Gravity, °API				54.2	34.3	20.0	9.1	15.1	16.3
Sulfur, W %				<0.02	0.14	0.71	1.44	1.17	1.10
Flash Point, °F								330	
Pour Point, °F								60	
Carbon, W %									84.84
Hydrogen, W %									11.19
Nitrogen, ppm									3550
Bromine No.				6.3	11.4				
Vis SFS @ 210°F								51	
RCR, W %							19.6		
Vanadium, ppm							156.0		
Nickel, ppm							57.0		

a. Calculated from correlation.

Table F-3. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	185-211-12
Catalyst Age, Bbl/Lb	0.43
Feed	Tia Juana Vacuum Bottoms
HRI No. (Feed)	2414
Catalyst	LX-22-3

OPERATING CONDITIONS

Hydrogen Pressure, psig	2005
Temperature, °F	791
Liquid Space Velocity, V/hr/V	0.47
Catalyst Space Velocity, B/D/Lb	0.035
Hydrogen Rate, SCF/B	4400
Reactor Type	Downflow
Hydrogen Consumption, SCF/B	653
975°F+ Conversion, V %	26

YIELDS									
Cut Points	H2S & NH3	C1-C3[a]	C4-C6[a]	IBP-400°F	400-650°F	650-975°F	975°F+	400°F+	Collected Liquid
W %	1.9	0.8	0.4	3.2	8.2	21.6	64.9	94.7	
V %			0.7	4.2	9.9	23.8	65.8	99.5	103.7
Gravity, °API				50.3	33.5	20.0	8.0	14.5	15.7
Sulfur, W %				< 0.02	0.23	0.75	1.92	1.51	1.32
Flash Point, °F								295	
Pour Point, °F								65	
Carbon, W %									86.83
Hydrogen, W %									11.54
Nitrogen, ppm									4380
Bromine No.				9.4	11.4				
Vis SFS @ 210°F								53	
RCR, W %							21.9		
Vanadium, ppm							268.0		
Nickel, ppm							74.0		

a. Calculated from correlation

Table F-4. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	184-173-4
Catalyst Age, Bbl/Lb	0.2
Feed	Gach Saran Vacuum Bottoms
HRI No. (Feed)	L-352
Catalyst	LX-22-2

OPERATING CONDITIONS

Hydrogen Pressure, psig	2020
Temperature, °F	790
Liquid Space Velocity, V/hr/V	0.73
Catalyst Space Velocity, B/D/Lb	0.055
Hydrogen Rate, SCF/B	4090
Reactor Type	Downflow
Hydrogen Consumption, SCF/B	770
975°F+ Conversion, V %	20

YIELDS

Cut Points	H_2S & NH_3	C_1-C_3[a]	C_4-C_6[a]	IBP-400°F	400-650°F	650-975°F	975°F+	400°F+	Collected Liquid
W %	2.6	0.8	0.4	2.3	6.0	21.2	67.8	95.0	
V %			0.7	3.2	7.3	23.6	70.8	101.7	104.9
Gravity, °API				50.2	32.9	19.6	10.4	15.8	16.7
Sulfur, W %				<0.02	0.10	0.72	1.39	1.16	1.08
Flash Point, °F								300	
Pour Point, °F								65	
Carbon, W %									86.73
Hydrogen, W %									10.93
Nitrogen, ppm									5800
Bromine No.				7.4	11.0				
Vis SFS @ 210°F								50	
RCR, W %							19.2		
Vanadium, ppm							56.0		
Nickel, ppm							63.0		

a. Calculated from correlation.

Table F-5. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	184-173-20
Catalyst Age, Bbl/Lb	1.31
Feed	Gach Saran Vacuum Bottoms
HRI No. (Feed)	L-352
Catalyst	LX-22-2

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	791
Liquid Space Velocity, V/hr/V	1.01
Catalyst Space Velocity, B/D/Lb	0.075
Hydrogen Rate, SCF/B	3990
Reactor Type	Downflow
Hydrogen Consumption, SCF/B	600
975°F+ Conversion, V %	25

YIELDS

Cut Points	H_2S & NH_3	C_1-C_3[a]	C_4-C_6[a]	IBP-400°F	400-650°F	650-975°F	975°F+	400°F+	Collected Liquid
W %	2.0	0.9	0.5	1.3	8.6	22.5	65.1	96.2	
V %			0.8	1.8	10.3	24.8	66.3	101.4	103.2
Gravity, °API				55.1	32.6	18.7	7.7	13.5	14.1
Sulfur, W %				< 0.02	0.47	0.92	2.14	1.71	1.61
Flash Point, °F								310	
Pour Point, °F								65	
Carbon, W %									85.16
Hydrogen, W %									10.72
Nitrogen, ppm									5700
Bromine No.				9.7	14.1				
Vis SFS @ 210°F								75	
RCR, W %								20.4	
Vanadium, ppm								114	
Nickel, ppm								88	

a. Calculated from correlation

Table F-6. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	185-216-6
Catalyst Age, Bbl/Lb	0.38
Feed	Bachaquero Vacuum Bottoms
HRI No. (Feed)	L-354
Catalyst	LX-22-3
OPERATING CONDITIONS	
Hydrogen Pressure, psig	2020
Temperature, °F	791
Liquid Space Velocity, V/hr/V	0.68
Catalyst Space Velocity, B/D/Lb	0.053
Hydrogen Rate, SCF/B	5956
Reactor Type	Downflow

YIELDS						
Cut Points	IBP- 400°F	400- 650°F	650- 975°F	975°F+	650°F+	Coll. Liquid
V %	3.3	11.7	24.0	61.0	85.0	100.0
Gravity, °API	44.3	31.3	19.8	6.0	9.8[a]	15.2
Sulfur, W %	< 0.02	0.24	0.66	1.69	1.42	1.26
Aniline Point, °F		148	172			
Pour Point, °F			40		70	
Bromine No.	10.3	11.8				
Vis SFS @ 210°F					97	
ASTM Color			D8.0			
RCR, W %				22.1		
Vanadium, ppm				262		
Nickel, ppm				95		

a. Calculated from fractions.

Table F-7. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	185-192-7
Catalyst Age, Bbl/Lb	0.309
Feed	Tia Juana Vacuum Bottoms
HRI No. (Feed)	2414
Catalyst	12 x 20 Mesh Porocel (HRI 2765)
OPERATING CONDITIONS	
Hydrogen Pressure, psig	2000
Temperature, °F	789
Liquid Space Velocity, V/hr/V	0.51
Catalyst Space Velocity, B/D/Lb	0.039
Hydrogen Rate, SCF/B	4250
Reactor Type	Downflow

YIELDS						
Cut Point	IBP 500°F	500-650°F	650-975°F	975°F+	650°F+	Coll. Liquid
V %	3.3	5.0	16.0	75.7	91.7	100.0
Gravity, °API	40.8	29.6	19.0	7.2	9.1[a]	10.6
Sulfur, W %	0.53	1.65	2.08	2.72	2.62[a]	2.52[a]
Aniline Point, °F		149	173			
Pour Point, °F			55		95	
Bromine No.	30.5	28.0				
Vis SFS @ 210°F					183	
ASTM Color			D8.0			
RCR, W %				21.9		
Vanadium, ppm				333		261
Nickel, ppm				80		60

[a] Calculated from fractions.

Table F-8. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	201-70-25
Catalyst Age, Bbl/Lb	2.619
Feed	Demetallized Bachaquero Vacuum Bottoms[a]
HRI No. (Feed)	L3-59
Catalyst	0.02" Beads (HRI 3104)

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	763
Liquid Space Velocity, V/hr/V	0.87
Catalyst Space Velocity, B/D/Lb	0.093
Hydrogen Rate, SCF/B	4810
Reactor Type	Downflow

YIELDS

Cut Points	C_1-C_3	C_4-C_6	IBP-500°F	500-650°F	650-975°F	975°F+	650°F+	Collected Liquid
W %	(0.8)	(0.3)						
V %			3.3	7.0	28.7	61.0[c]	89.3	100.0
Gravity, °API			37.1	29.8	21.1	8.0	11.1[b]	14.9
Sulfur, W %			<0.02	< 0.02	0.06	0.95	0.68[b]	0.62[b]
Aniline Point, °F				140	175			
Pour Point, °F					60		60	
Bromine No.			5.7	6.8				
Vis SFS @ 210°F							63	
ASTM Color					L6.5			
RCR, W %						20.1		
Vanadium, ppm						251		
Nickel, ppm						82		

a. Demetallized over LX-22
b. Calculated from fractions
c. Results questionable.

Table F-9. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	185-219-4
Catalyst Age, Bbl/Lb	0.32
Feed	Demetallized Tia Juana Vacuum[a]
HRI No. (Feed)	L-361
Catalyst	0.02" Beads (HRI 3104)
OPERATING CONDITIONS	
Hydrogen Pressure, psig	2000
Temperature, °F	760
Liquid Space Velocity, V/hr/V	0.74
Catalyst Space Velocity, B/D/Lb	0.079
Hydrogen Rate, SCF/B	5850
Reactor Type	Downflow

YIELDS

Cut Points	IBP-500°F	500-650°F	650-975°F	975°F+	650°F+	Coll. Liquid
V %	4.0	8.7	26.7	60.6	87.3	100.0
Gravity, °API	37.8	30.2	21.4	13.2	15.6[b]	17.2
Sulfur, W %	0.02	0.02	0.02	0.69	0.49[b]	0.43[b]
Aniline Point, °F		148	182			
Pour Point, °F			55		50	
Bromine No.	3.4	4.2				
Vis SFS @ 210°F					68	
ASTM Color			D8.0			
RCR, W %				17.6		
Vanadium, ppm				302		
Nickel, ppm				64		

a. Demetallized over Porocel.
b. Calculated from fractions.

Table F-10. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	184-175-29
Catalyst Age, Bbl/Lb	3.087
Feed	Demetallized Tia Juana Vacuum Bottoms[a]
HRI No. (Feed)	L-357
Catalyst	0.02" Beads (HRI 3104)

OPERATING CONDITIONS

Hydrogen Pressure, psig	1990
Temperature, °F	760
Liquid Space Velocity, V/hr/V	0.92
Catalyst Space Velocity, B/D/Lb	0.098
Hydrogen Rate, SCF/B	4527
Reactor Type	Downflow

YIELDS

Cut Points	C_1-C_3	C_4-C_6	IBP-500°F	500-650°F	650-975°F	975°F+	650°F+	Collected Liquid
W %	(0.7)	(0.4)						
V %			3.0	7.0	30.0	60.0	90.0	100.0
Gravity, °API			39.5	30.1	21.3	10.9	14.2[b]	15.9[b]
Sulfur, W %			<0.02	<0.02	0.10	0.98	0.70[b]	0.64[b]
Aniline Point, °F				143	180			
Pour Point, °F					45		55	
Bromine No.			4.63	5.84				
Vis SFS @ 210°F							70	
ASTM Color					08.0			
RCR, W %						19.9		
Vanadium, ppm						226		150
Nickel, ppm						65		39

a. Demetallized over LX-22
b. Calculated from fractions.

Table F-11. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	185-218-4
Catalyst Age, Bbl/Lb	0.44
Feed	Demetallized Gach Saran Vacuum Bottoms[a]
HRI No. (Feed)	L-360
Catalyst	0.02" Beads (HRI 3104)
OPERATING CONDITIONS	
Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, V/hr/V	1.04
Catalyst Space Velocity, B/D/Lb	0.110
Hydrogen Rate, SCF/B	4140
Reactor Type	Downflow

YIELDS						
Cut Points	IBP-500°F	500-650°F	650-975°F	975°F+	650°F	Coll. Liquid
V %	4.7	10.0	29.3	56.0	85.3	100.0
Gravity, °API	37.9	30.3	20.7	9.7	13.3[b]	15.9[b]
Sulfur, W %	<0.02	<0.02	<0.02	0.54		
Aniline Point, °F		147	176			
Pour Point, °F			60		45	
Bromine No.	5.3	5.5				
Vis SUS @ 210°F					364	
ASTM Color			D8.0			
RCR, W %				16.4		
Vanadium, ppm				66		40
Nickel, ppm				57		29

a. Demetallized over Porocel.
b. Calculated from fractions.

Table F-12. OPERATING CONDITIONS, YIELDS, AND PRODUCT INSPECTIONS

Run No.	201-69-23
Catalyst Age, Bbl/Lb	2.52
Feed	Demetallized Gach Saran Vacuum Bottoms[a]
HRI No. (Feed)	L-356
Catalyst	0.02" Beads (HRI 3104)

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	759
Liquid Space Velocity, V/hr/V	1.07
Catalyst Space Velocity, B/D/Lb	0.111
Hydrogen Rate, SCF/B	9147
Reactor Type	Downflow

YIELDS

Cut Point	C_1-C_3	C_4-C_6	IBP-500°F	500-650°F	650-975°F	975°F+	650°F+	Collected Liquid
W %	(0.4)	(0.3)						
V %			3.3	6.0	28.0	62.7	90.7	100.0
Gravity, °API			38.4	28.7	20.2	10.7	13.5[b]	15.7
Sulfur, W %			< 0.02	< 0.02	0.07	0.80	0.59[b]	0.52[b]
Aniline Point, °F				142	176			
Pour Point, °F					75		55	
Bromine No.			8.5	8.0				
Vis SFS @ 122°F							935	
ASTM Color					08.0			
RCR, W %						16.8		
Vanadium, ppm						63		45
Nickel, ppm						62		36

a. Feed demetallized over LX-22
b. Calculated from fractions.

APPENDIX G

CONVERSION TABLE

APPENDIX G

CONVERSION TABLE

Variable	British Units	Metric Units	Conversion Factor
Temperature	Degrees Fahrenheit, °F	Degrees Centigrade, °C	°C = 5/9(°F-32)
Pressure	Pounds per Square Inch Gauge, psig	Kilograms per Square Centimeter, Kg/cm^2	$Kg/cm^2 = \frac{psig}{14.22}$
Hydrogen Rate	Standard Cubic Feet per Barrel, (60°F, 1 Atm.)	Normal Cubic Meters per Cubic Meter, NM^3/M^3 (0°C, 760 mm Hg)	$NM^3/M^3 = 0.168(SCF/Bbl)$

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APPENDIX H

GLOSSARY

1 Micron	10^4 Angstroms
g/cc	Grams/cubic centimeter
M^2/g	Square meters/gram
Mesh Sizes	Mesh sizes are all United States Standard Sieve Series
psig	Pounds per square inch, gauge
SCF/Bbl	Standard cubic feet of gas per barrel of oil (60°F, 1 Atm.)
$V_o/hr/V_r$	Volumes of oil/hour/volume of reactor
C.S.V.	Catalyst space velocity, barrels of oil/day/pound of catalyst
Bbl/Day/Lb	Barrels of oil/day/pound of catalyst
100X	Magnification of 100 times
200X	Magnification of 200 times
B/D	Barrels per day
ppm	Parts per million
SFS	Saybolt Furol Seconds
V.B.	Vacuum Bottoms = Vacuum Residuum

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